

1602 E 02

MISA

Water Quality

---

**STOPPING  
WATER POLLUTION  
AT ITS SOURCE**



---

**ST. CLAIR RIVER MISA  
PILOT SITE INVESTIGATION**

**VOLUME II**

**PART II – DETAILED TECHNICAL FINDINGS**

---



**Environment  
Ontario**

---



ISBN 0-7729-6304-5  
(3 Volume set)  
0-7729-6306-1  
(Part I)

ST. CLAIR RIVER MISA PILOT SITE INVESTIGATION

VOLUME II  
PART II - DETAILED TECHNICAL FINDINGS

Prepared by the  
St. Clair River MISA Pilot Site Team

JANUARY 1991



Cette publication technique  
n'est disponible qu'en anglais

Copyright: Queen's Printer for Ontario, 1990  
This publication may be reproduced for non-commercial purposes  
with appropriate attribution

PIBS  
log 88-2320-043





## FOREWORD

This report comprises Volume II, part II of the St. Clair River MISA Pilot Site investigation. A preliminary report of findings (Volume I) was previously released by the Ministry of the Environment in November 1987. Volume II, Parts I and III comprise the Technical Summary and Appendices respectively and are published separately.

This document presents a detailed discussion of results from each of the monitoring components applied during the Pilot site investigation. Each of these components can be classified into one of four more general categories including: i) effluent monitoring, ii) ambient monitoring iii) biological monitoring and iv) modelling.

This report provides additional discussion of specific chemicals of concern as well as rationale for their selection and results of water-, sediment- and biologically-based load allocation procedures.

Copies of parts I and III are available from the Ministry of the Environment, Water Resources Branch.

## ACKNOWLEDGEMENTS

The completion of a study of this magnitude required the input and cooperation of many different individuals and organizations. The authors would particularly like to recognize the efforts of Mr. C.F. Schenk (retired) of the Water Resources Branch for his encouragement and innovative approach to establishing discharge standards which more precisely reflect water quality considerations.

Initial direction, planning and coordination was provided by Mr. Y.S. Hamdy of the Water Resources Branch. His keen foresight enabled the development of the novel yet workable investigative techniques.

Field support and sample collections were provided by staff of the Great Lakes and Aquatic Biology Sections, of the Water Resources Branch. Special thanks go to Emery Law and his staff from the Great Lakes Section for their dedicated work in the field. Staff of the Southwestern Regional Office and Sarnia District Office of the Ontario Ministry of the Environment assisted in key advisory roles as well as providing significant field support.

Laboratory analyses were conducted by staff of the Laboratory Services Branch and the Southwestern Region of the Ministry of the Environment in Rexdale, and London, Ontario respectively. Their cooperation and assistance in analysing the large sample load is greatly appreciated.

Valuable direction and comments were provided by Mr. F.C. Fleischer and Mr. R.J. Boone of the Great Lakes Section; Mr. P. Dennis, Water Quality Policy Coordinator; Dr. T. Tuszynski of the MISA Industrial Section, Mr. G. Rutherford of the Water Resources Branch and members of the St. Clair River MISA Pilot Site team.

Thanks are also extended to Dr. D. Spry and Mr. C. de Barros of the Aquatic Biology Section and Mr. R. Angelow of the Hazardous Contaminants Coordination Branch for their efforts in assembling water quality criteria.

Electronic data processing and graphics were provided by a number of groups, in particular, staff of the Great Lakes Section, Dr. J.A. McCorquodale of the University of Windsor and C. Luck of Graphic Tactics.

The text was typed by a number of individuals from the Water Resources Branch including V.E. Sokolyk, E. Lacson, C. Fong, L. Satya, L. Matar and A. Foley.

## PILOT SITE TEAM MEMBERS

The St. Clair River MISA pilot site team consisted of:

S. Abernethy, Water Resources Branch, MOE  
R. Boone, Water Resources Branch, MOE  
D. Edwardson, Detroit, St. Clair, St. Marys River Improvement Team, MOE  
R. Griffiths, Southwestern Region, MOE  
K. Haniff, Detroit, St. Clair, St. Marys River Improvement Team, MOE  
B. Hawkins, Southwestern Region, MOE  
A. Hayton, Water Resources Branch, MOE  
M. Jackson, Water Resources Branch, MOE  
A. Johnson, Water Resources Branch, MOE  
G. Johnson\*, Coordinator, Water Resources Branch, MOE  
J. Lee, Water Resources Branch, MOE  
T. Lomas, Water Resources Branch, MOE  
J. Luyt, Sarnia Area, MOE  
J.A McCorquodale, University of Windsor  
P. Nettleton, Water Resources Branch, MOE  
A. Mudroch\*\*, National Water Research Institute, DOE  
A. Rodrigues, Water Resources Branch, MOE  
D. Rokosh, Water Resources Branch, MOE  
W. Scheider, Water Resources Branch, MOE  
K. Suns, Water Resources Branch, MOE  
S. Thornley, Southwestern Region, MOE  
D. Veal, Southwestern Region, MOE  
G. Westlake, Water Resources Branch, MOE

\* Replaced Y. Hamdy

\*\* Replaced K. Rodgers

## SYNTHESIS TEAM MEMBERS

The following individuals comprised the synthesis writing team and were responsible for writing, editing and for assembling significant portions of this report.

G. Johnson - Editor

R. Boone

J.A. McCorquodale

P. Nettleton

W. Scheider

D. Veal

## TABLE OF CONTENTS

	<u>PAGE</u>
Foreword.....	i
Acknowledgements.....	ii
Pilot Site Team Members.....	iv
Synthesis Team Members.....	v
List of Tables.....	ix
List of Figures.....	xiii
List of Appendices.....	xxii
 1.0 INTRODUCTION.....	 I-1
1.1 Overview of the MISA Initiative.....	I-1
1.2 Development of Water Quality-Based Effluent Limits.....	 I-2
1.3 The St. Clair River Pilot Site Study.....	I-3
 2.0 SITE DESCRIPTION.....	 II-1
2.1 Description of the Pilot Site Study Area.....	II-1
2.1.1 Hydrology of the St. Clair River.....	II-1
2.1.2 Area Land and Water Uses.....	II-1
2.1.3 Geology and Soils.....	II-4
2.2 Description of Point Sources.....	II-5
2.2.1 Dow Chemical Canada Inc., Sarnia Division.....	II-5
2.2.2 Polysar Ltd., Sarnia.....	II-9
2.2.3 The Cole drain and Area Landfills.....	II-11
2.3 Description of Non-Point Sources.....	II-14
2.3.1 Combined Sewer Overflows.....	II-15
 3.0 STUDY OUTLINE.....	 III-1
3.1 Study Overview.....	III-1
3.2 Description of Monitoring Strategies.....	III-2
3.2.1 Sediment/Benthos Monitoring and Evaluation.....	III-2
3.2.2 Biota Monitoring and Evaluation.....	III-2
3.2.3 Effluent Monitoring and Evaluation.....	III-3
3.2.4 Water Column Monitoring and Evaluation.....	III-4

## TABLE OF CONTENTS (Cont'd)

	<u>PAGE</u>
4.0 METHODOLOGY AND DISCUSSION OF RESULTS FOR SPECIFIC MEDIA	
4.1 Effluent Monitoring.....	IV-1
4.1.1 Long-Term Effluent Monitoring.....	IV-1
4.1.2 Centrifugation of Whole Effluent.....	IV-48
4.1.3 Sequential Sampling - Calibration and Testing of the WASTOX Model.....	IV-49
4.1.4 Effluent Toxicity.....	IV-86
4.2 Ambient Water Quality Monitoring.....	IV-89
4.2.1 Centrifugation.....	IV-89
4.2.2 Investigative Water Sampling.....	IV-116
4.3 Sediment Quality Monitoring.....	IV-136
4.3.1 Sediment Contaminant Distribution.....	IV-136
4.3.2 Sediment Toxicity.....	IV-163
4.4 Biological Monitoring.....	IV-170
4.4.1 Heterotrophic Bacteria.....	IV-170
4.4.2 Bacterial Slimes.....	IV-172
4.4.3 Phytoplankton (total seston).....	IV-175
4.4.4 <u>Cladophora</u> .....	IV-181
4.4.5 Macrophytes.....	IV-184
4.4.6 Benthic Invertebrate Enumeration.....	IV-189
4.4.7 In-Place Pollutants: Benthic Contaminant Residues.....	IV-204
4.4.8 Caged Clams.....	IV-213
4.4.9 Juvenile Fish.....	IV-230
4.4.10 Sportfish.....	IV-237
4.4.11 Mutagenicity Testing.....	IV-245
5.0 DISCUSSION OF RESULTS FOR SPECIFIC CHEMICALS OF CONCERN	
5.1 Rationale for Selection of Compounds.....	V-1
5.2 Documentation of Sources.....	V-5
5.3 Occurrence in the Environment - Discussion on a Chemical Specific Basis.....	V-8

## TABLE OF CONTENTS (Cont'd)

	<u>PAGE</u>
6.0 ST. CLAIR RIVER LOAD ALLOCATION.....	VI-1
6.1 Purpose.....	VI-1
6.2 Introduction.....	VI-1
6.2.1 Description of Models Used.....	VI-3
6.3 Mixing Zone Definition.....	VI-44
6.4 Environmental Quality Criteria Considered for Use.....	VI-45
6.5 Statistical Considerations in Developing Load Allocations.....	VI-47
6.6 Load Allocation Procedures.....	VI-62
6.6.1 Water-Based Load Allocation.....	VI-62
6.6.2 Biota-Based Load Allocation.....	VI-72
6.6.3 Sediment-Based Load Allocation.....	VI-81
6.7 Technique Assessment.....	VI-91
6.7.1 Model Development.....	VI-91
6.7.2 Interpretation of Model Results.....	VI-93
6.7.3 Technique Utility within MISA.....	VI-94
6.7.4 Technique Applicability.....	VI-96
7.0 CRITIQUE OF ASSESSMENT PROCEDURES.....	VII-1
7.1 Critique of Component Studies from the Modeling View point.....	VII-1
7.1.1 Effluent Monitoring.....	VII-1
7.1.2 Ambient Monitoring.....	VII-2
7.1.3 Biological Monitoring.....	VII-4
8.0 CONCLUSIONS AND RECOMMENDATIONS.....	VIII-1
9.0 REFERENCES.....	IX-1



## LIST OF TABLES

<u>TABLE</u>	<u>PAGE</u>
4.1.1 Effluent/Water Quality Parameter List.....	IV-2
4.1.2 Long Term Effluent Monitoring Results.....	IV-8
4.1.3 Long-Term Effluent Monitoring: Summary of Non-Parametric ANOVA Results for Statistically Significant Differences Between Seasons (May 1986-March 1987).....	IV-17
4.1.4 Parameters Exhibiting Visual Trends (increasing or decreasing) with Time, Confirmed by Statistically Significant ( $P < 0.05$ ) Differences Identified in Effluent Quality at Measured Sewers (May 1986-March 1987).....	IV-18
4.1.5 Loadings of Compounds (g/day) Entering the St. Clair River from the Cole drain and Dow Chemical Sewers: 1985, 1986/87 - Chlorinated Aromatics.....	IV-25
4.1.6 Loadings of Compounds (kg/day) Entering the St. Clair From the Cole drain and Dow Chemical sewers: 1985, 1986/1987 - Volatiles.....	IV-26
4.1.7 Average Point Source Loadings as a Percentage of Loadings from the Dow 42-inch Sewer.....	IV-29
4.1.8 Spearman Rank Correlation Results: Coefficient (Significance).....	IV-43
4.1.9 Chemical and Physical Properties of Contaminants.....	IV-66
4.1.10 Statistical Comparison of Concentrations in Sampled Cell...	IV-82
4.1.11(a) Ratio of Measured to Predicted Concentrations for All Runs - Raw Data.....	IV-87
4.1.11(b) Ratio of Measured to Predicted Concentrations for All Runs - Plume Effect.....	IV-87
4.1.11(c) Ratio of measured to Predicted Concentrations for All Runs - Plume S.G. Mass Balance.....	IV-87
4.1.12 Results of 96 hr. Static Acute Lethality Test on Whole Effluents of Dow.....	IV-88

## LIST OF TABLES (Cont'd)

<u>TABLE</u>	<u>PAGE</u>
4.2.1 Centrifuging Sampling Locations.....	IV-92
4.2.2 Centrifuged Solids Parameter List.....	IV-93
4.2.3 Partitioning of Contaminants Between Aqueous and Solid Phases.....	IV-95
4.2.4 Ambient Water Investigative Sampling Locations.....	IV-119
4.2.5 Samples Exceeding Water Quality Criteria for Selected Parameters by Survey.....	IV-126
4.2.6 Frequency of Samples in Excess of Method Detection Limits (MDL) and Water Quality Objectives (WQO).....	IV-127
4.2.7 Samples Measured Above Detection Limits for Selected Parameters by Cruise and Depth.....	IV-131
4.3.1 Sediment Bioassessment Results from the St. Clair River....	IV-166
4.4.1 Heterotrophic Bacterial Results from the St. Clair River (Ecosystem Stations) August 26, 1986.....	IV-173
4.4.2 Contaminants Found in Seston Samples Obtained from the St. Clair River - July 30, 1986.....	IV-177
4.4.3 Concentration of OCS, HCB and HC8D (ng/g) Dry Weight in Cladophora Sampled in the St. Clair River in July and September 1986.....	IV-185
4.4.4 Summary of the Analytical Results for Macrophyte Samples Collected from the St. Clair River - September 23, 1986.....	IV-190
4.4.5 Species Composition (Mean Number per 516 cm <sup>2</sup> ) of Benthic Communities 1-7 in the St. Clair River, May 1985. (P denotes a Mean Density of Less than 1 Individual per sample).....	IV-195

## LIST OF TABLES (Cont'd)

<u>TABLE</u>		<u>PAGE</u>
4.4.6	Mean Values of Physiochemical Sediment Variables Associated with Benthic Communities 1-7 from the St. Clair River, May 1985. All values are expressed in mg/kg unless otherwise stated.....	IV-200
4.4.7	Occurrence (%) and Maximum Measured Concentrations (µg/kg dry weight) of Organochlorine Compounds in Sediments Associated with Benthic Communities in the St. Clair River, May 1985.....	IV-201
4.4.8	In-Place Pollutants Sampling Locations and Sample Types Collected.....	IV-205
4.4.9	Concentrations of HCB in Bottom Water (ng/L), Bulk Sediment (ng/g Dry Wt.), Hexagenia (ng/g Wet Wt.) and Sculpin (ng/g Wet Wt.).....	IV-208
4.4.10	Concentrations of HCB in Bottom Water (ng/L), Bulk Sediment (ng/g Dry Wt.), Hexagenia (ng/g Wet Wt.), and Sculpin (ng/g Wet Wt.).....	IV-209
4.4.11	Concentrations of OCS in Bottom Water (ng/L), Bulk Sediment (ng/g Dry Wt.), Hexagenia (ng/g Wet Wt.), and Sculpin (ng/g Wet Wt.).....	IV-211
4.4.12	Clam Tissue Parameter List.....	IV-216
4.4.13	Clam Retrievals and Observations.....	IV-219
4.4.14	1986 MISA Clam Exposure Stations: Location and Physical Characteristics.....	IV-220
4.4.15	Mean Clam Tissue Concentrations for Selected Contaminants (ng/g).....	IV-223
4.4.16	Chlorinated Organic Residues in Young-of-the-Year Spottail Shiners from the Clair River, Lake St. Clair and Lake Huron (values in ng/g, means with SD, Wet Weight).....	IV-232

## LIST OF TABLES (Cont'd)

<u>TABLE</u>	<u>PAGE</u>
4.4.17 Volatile Hydrocarbon Residues in Young-of-the-Year Emerald Shiners from the St. Clair River (ng/g wet wt.)...	IV-233
4.4.18 Mutagenicity Testing Results, Fluctuation Assay, of Dow Chemical and Polysar Effluents.....	IV-247
5.1.1 Production and Use of Chemicals of Potential Concern.....	V-2
5.1.2 Selected Parameters of Potential Concern: Physical/ Chemical Characteristics.....	V-3
5.1.3 Selected Parameters of Potential Concern: Summary of Aquatic Toxicological Information.....	V-4
5.3.1 Frequency of Exceedence of Media-Specific Criteria From Samples Obtained: a) between Polysar and Suncor; b) in the remainder of the river (1986).....	V-14
6.2.1 Mixing Zone Definition.....	VI-2
6.2.2 Parameter values for HCB Food Chain Simulation.....	VI-29
6.2.3 Parameter Values for OCS Food Chain Simulation.....	VI-30
6.2.4 Sensitivity Analysis for Sportfish Model Parameters.....	VI-42
6.4.1 Suggested Water Quality Criteria.....	VI-48
6.4.2 Existing and Calculated Criteria for Biota and Sediment.....	VI-49
6.6.1 Water Based Load Allocation Summary for HCB.....	VI-68
6.6.2 Biota Based Load Allocation Summary for HCB.....	VI-83
6.6.3 Sediment Based Load Allocation Summary for HCB.....	VI-86
7.1.1 Utility of Various Techniques for Establishing Effluent Limits.....	VII-5

## LIST OF FIGURES

<u>FIGURE</u>	<u>PAGE</u>
2.1 Intakes/outfalls.....	II-2
2.2 The St. Clair River.....	II-3
4.1.1 Twice-Weekly Effluent Monitoring Results - Hexachlorobenzene.....	IV-9
4.1.2 Twice-Weekly Effluent Monitoring Results - Hexachlorobutadiene.....	IV-10
4.1.3 Twice-Weekly Effluent Monitoring Results - Octachlorostyrene.....	IV-11
4.1.4 Twice-Weekly Effluent Monitoring Results - Hexachloroethane.....	IV-12
4.1.5 Twice-Weekly Effluent Monitoring Results - 2,4,5-Trichlorotoluene.....	IV-13
4.1.6 Twice-Weekly Effluent Monitoring Results - Tetrachloroethylene.....	IV-14
4.1.7 Twice-Weekly Effluent Monitoring Results - Carbon Tetrachloride.....	IV-15
4.1.8 Results of Non-Parametric ANOVA - Polysar 72-inch sewer.....	IV-19
4.1.9 Results of Non-Parametric ANOVA - Dow 42-inch sewer.....	IV-20
4.1.10 Results of Non-parametric ANOVA - 48-, 54-inch sewers.....	IV-21
4.1.11 Results of Non-parametric ANOVA - Dow 3rd St. sewer.....	IV-22
4.1.12 Results of Non-parametric ANOVA - Dow 4th St. sewer.....	IV-23
4.1.13a Total Chlorinated Aromatic Loadings Entering the St. Clair River from the Cole drain and Dow Chemical Sewers (g/day)....	IV-30
4.1.13b Total Volatile Organic Loadings Entering the St. Clair River from the Cole drain and Dow Chemical Sewers (g/day)....	IV-30
4.1.14a Total Chlorinated Aromatic Loadings to the St. Clair River from Dow Chemical 1985 to 1987 (g/day).....	IV-31
4.1.14b Total Volatile Organic Loadings to the St. Clair River from Dow Chemical 1985 to 1987 (kg/day).....	IV-31
4.1.15 Weekly Effluent Loadings - Cole drain.....	IV-32
4.1.16 Weekly Effluent Loadings - Dow 42-inch.....	IV-33
4.1.17 Weekly Effluent Loadings - Dow 42-inch.....	IV-34
4.1.18 Weekly Effluent Loadings - Dow 42-inch.....	IV-35
4.1.19 Weekly Effluent Loadings - Dow 4th St.....	IV-36
4.1.20 Weekly Effluent Loadings - Dow 4th St.....	IV-37

## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
4.1.21 Weekly Effluent Loadings - Dow 42-inch, 4th St.....	IV-38
4.1.22 Monthly Summary of Loadings at Block 90 Pond Outlet (kg/day).....	IV-46
4.1.23 Sequential Sampling Intakes/Outfalls.....	IV-54
4.1.24 Sequential Sampling Ambient Stations.....	IV-55
4.1.25 Fine Grid/Coarse Definition for the St. Clair River.....	IV-58
4.1.26 Fine Grid Definition for the St. Clair River.....	IV-59
4.1.27 "Fine Grid" Flow Pattern (showing locations of 1985 HCB Loads).....	IV-60
4.1.28 Coarse Grid Cell Definition for the Wastox Model with 1985 HCB Loads.....	IV-62
4.1.29 Coarse Grid Flow Distribution in the St. Clair River Delta..	IV-63
4.1.30 A Typical Cell in WASTOX and TOXIWASP Models.....	IV-64
4.1.31 St. Clair River Sequential Sampling Stn. 204 / 215 / 42-inch sewer.....	IV-68
4.1.32 St. Clair River Sequential Sampling Stn. 217 / 4th St. sewer.....	IV-69
4.1.33 St. Clair River Sequential Sampling Stn. 203 / 204 / Cole drain.....	IV-70
4.1.34 St. Clair River Sequential Sampling Stn. 204 / 215 / 42-inch sewer.....	IV-71
4.1.35 St. Clair River Sequential Sampling Stn. 204 / 211 / 42-inch sewer.....	IV-72
4.1.36 Load Frequency Distribution Curve for HCB for 1986 Sequential Data.....	IV-73
4.1.37 Comparison of Ratios of the Measured to the Predicted Concentrations for HCB and HCE for Cells 5, 10, 12 and 18 for the Spring, Summer and Fall Cruises.....	IV-77
4.1.38 Comparison of the Ratios of the Measured to the Predicted Concentrations for PERC, Carbon Tetrachloride and HCBd.....	IV-78
4.1.39 St. Clair River - WASTOX - Fine Grid HCB Concentration in Spring.....	IV-79
4.1.40 St. Clair River - WASTOX - Fine Grid HCE Concentration in Spring.....	IV-80



## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
4.2.1 St. Clair River Ambient Centrifuging Stations.....	IV-91
4.2.2 Whole Effluent/Water Contaminant Load Accounted for by Suspended/Aqueous Fractions (Hexachlorobenzene).....	IV-96
4.2.3 Whole Effluent/Water Contaminant Load Accounted for by Suspended/Aqueous Fractions (Tetrachloroethylene).....	IV-96
4.2.4 Whole Effluent/Water Contaminant Load Accounted for by Suspended/Aqueous Fractions (Hexachlorobutadiene).....	IV-97
4.2.5a Removal Efficiency vs. % Fines.....	IV-100
4.2.5b Size Fractionation for Centrifuged Solids.....	IV-101
4.2.6 Phosphorus on Suspended Solids ANOVA Boxplot (95% C.I.)....	IV-105
4.2.7 Mercury on Suspended Solids ANOVA Boxplot (95% C.I.).....	IV-106
4.2.8 HCB on Suspended Solids ANOVA Boxplot (95% C.I.).....	IV-107
4.2.9 HCB on Suspended Solids ANOVA Boxplot (95% C.I.).....	IV-108
4.2.10 1,2,3,4-TCB on Suspended Solids ANOVA Boxplot (95% C.I.)....	IV-109
4.2.11 QCB on Suspended Solids ANOVA Boxplot (95% C.I.).....	IV-110
4.2.12 HCB on Suspended Solids ANOVA Boxplot (95% C.I.).....	IV-113
4.2.13 HCB on Suspended Solids ANOVA Boxplot (95% C.I.).....	IV-114
4.2.14 QCB on Suspended Solids ANOVA Boxplot (95% C.I.).....	IV-115
4.2.15 Ambient Water Investigative Sampling Locations.....	IV-120
4.2.16 Chloride Distribution in the St. Clair River (mg/L).....	IV-124
4.2.17 Conductivity in the St. Clair River (umho/cm).....	IV-124
4.2.18 Frequency of Samples Above Method Detection Limits (MDL)....	IV-128
4.2.19 Tetrachloroethylene Distribution in the St. Clair River (µg/L).....	IV-129
4.2.20 Carbon Tetrachloride Distribution in the St. Clair River (ug/L).....	IV-129
4.2.21 Hexachlorobenzene Distribution in the St. Clair River (ng/L)	IV-132
4.2.22 Octachlorostyrene Distribution in the St. Clair River (ng/L)	IV-132
4.2.23 Hexachloroethane Distribution in the St. Clair River (ng/L).	IV-133
4.3.1 St. Clair River Sediment Sampling Stations.....	IV-137

## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
4.3.2 Al and Fe Concentrations in Sediments from the St. Clair River.....	IV-139
4.3.3 Mg and Mn Concentrations in Sediments from the St. Clair River.....	IV-140
4.3.4 Cr and Pb Concentrations in the Sediments from the St. Clair River.....	IV-141
4.3.5 Cu and Ni Concentrations in Sediments from the St. Clair River.....	IV-142
4.3.6 Zn and Cd Concentrations in Sediments from the St. Clair River.....	IV-143
4.3.7 Hg and Co Concentrations in Sediments from the St. Clair River.....	IV-144
4.3.8 Al and Fe Concentrations in Sediments Collected Along a Transect Across the St. Clair River.....	IV-146
4.3.9 Mg and Mn Concentrations in Sediments Collected Along a Transect Across the St. Clair River.....	IV-147
4.3.10 Cr and Pb Concentrations in Sediments Collected Along a Transect Across the St. Clair River.....	IV-149
4.3.11 Cu and Ni Concentrations in Sediments Collected Along a Transect Across the St. Clair River.....	IV-150
4.3.12 Zn and Cd Concentrations in Sediments Collected Along a Transect Across the St. Clair River.....	IV-151
4.3.13 Hg and Co Concentrations in Sediments Collected Along a Transect Across the St. Clair River.....	IV-152
4.3.14 PCB's and Hexachlorobenzene Concentrations in St. Clair River Sediments.....	IV-153
4.3.15 Hexachlorobutadiene and Hexachloroethane Concentrations in St. Clair River sediments.....	IV-154
4.3.16 Octachlorostyrene and Pentachlorobenzene Concentrations in St. Clair River Sediments.....	IV-155
4.3.17 Tri-and Tetrachlorobenzene Concentrations in St. Clair River Sediments.....	IV-156
4.3.18 Tri-and Tetrachlorobenzene Concentrations in St. Clair River Sediments.....	IV-157
4.3.19 Location of Sediment Bioassay Collection Sites in the St. Clair River.....	IV-164



## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
4.4.1 Ecosystem Station Sampling Locations.....	IV-171
4.4.2 St. Clair River Chlorophyll <u>a</u> Station, 1986.....	IV-179
4.4.3 Summary of Secchi Disc Chlorophyll <u>a</u> Data: St. Clair River, 1986.....	IV-180
4.4.4 St. Clair River <u>Cladophora</u> Sampling Sites, 1986.....	IV-182
4.4.5 St. Clair River, Macrophyte Collection Sites, 1986.....	IV-188
4.4.6a Interpretation of Benthic Invertebrate Communities 1-7 in Terms of Environmental Quality and Habitat.....	IV-198
4.4.6b May 1985 Benthic Study Station Locations; Distribution of Benthic Invertebrate Communities in the St. Clair River.....	IV-199
4.4.7 Environmental Quality Zones in the St. Clair River Based on the Distribution of Benthic Fauna (May 1985).....	IV-202
4.4.8 Distribution of Environmental Quality Zones in the St. Clair River in the Spring of 1977 and 1985.....	IV-203
4.4.9 In-Place Pollutants Sampling Locations.....	IV-206
4.4.10 Relationship Between [HCB] in Sediments and [HCB] in <u>Hexagenia</u> .....	IV-210
4.4.11 Relationship Between [OCS] in Sediments and [OCS] in <u>Hexagenia</u> .....	IV-212
4.4.12 Caged Clam Sampling Stations.....	IV-214
4.4.13 St. Clair River MISA Clam Study: Hexachlorobenzene (ng/g); Hexachlorobutadiene (ng/g).....	IV-224
4.4.14 St. Clair River MISA Clam Study: Benzene (ng/g); Ethylbenzene (ng/g).....	IV-226
4.4.15 St. Clair River MISA Clam Study: Perchloroethylene (ng/g); m-,o-,p-Xylene (ng/g).....	IV-227
4.4.16 Juvenile Fish Collection Sites in the St. Clair River and Lakes Huron and St. Clair.....	IV-231
4.4.17 Hexachlorobenzene Residue Trends in Young-of-the-Year Spottail Shiners for the St. Clair River at Lambton Generating Station (Mean $\pm$ 95% C.L.).....	IV-235

## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
4.4.18 Octachlorostyrene Residue Trends in Young-of-the-Year Spottail Shiners for the St. Clair River at the Lambton Power Generation Station (Mean $\pm$ 95% C.L.).....	IV-236
4.4.19 HCB in Carp from Lakes Huron, St. Clair and the St. Clair River.....	IV-239
4.4.20 HCB in Channel Catfish from Lakes Huron, St. Clair and the St. Clair River.....	IV-242
4.4.21 OCS in Carp from Lakes Huron, St. Clair and the St. Clair River.....	IV-243
4.4.22 OCS in Channel Catfish from Lakes Huron, St. Clair and the St. Clair River.....	IV-244
5.3.1 Comparison of Parameters of Concern in the St. Clair River from Polysar to Suncor by Media (Max, Mean, Min): OCS, PERC..	V-10
5.3.2 Comparison of Parameters of Concern in the St. Clair River from Polysar to Suncor by Media (Max, Mean, Min): HCB, HCBd..	V-11
5.3.3 Distribution of Hexachlorobenzene in Water, Sediments and Biomonitors Along the Ontario Shoreline of the St. Clair River.....	V-16
5.3.4 Distribution of Hexachlorobutadiene in Water, Sediments and Biomonitors Along the Ontario Shoreline of the St. Clair River.....	V-20
5.3.5 Distribution of Octachlorostyrene in Water, Sediments and Biomonitors Along the Ontario Shoreline of the St. Clair River.....	V-24
5.3.6 Distribution of Tetrachloroethylene in Water, Sediments and Biomonitors Along the Ontario Shoreline of the St. Clair River.....	V-30
6.2.1 Definition of Reaches for the KETOX Model for the St. Clair River.....	VI-5
6.2.2 Schematic of the St. Clair River for the KETOX model.....	VI-6
6.2.3 KETOX Panel Showing the Outfalls.....	VI-7
6.2.4 Effect of Lateral Dispersion on Concentration Profile at Stag Island.....	VI-9
6.2.5 Effect of River Flow on Ambient Concentrations and Plume Width.....	VI-11

## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
6.2.6 The Effect of Partition Coefficient and Suspended Solids on Dissolved Fraction.....	VI-12
6.2.7 Effect of Active Bed Thickness on Bed Response Time for HCB with Bed Decay Rate of 10 1/s.....	VI-14
6.2.8 Effect of Bed Diffusion Processes on the Bed Response for HCB..	VI-15
6.2.9 Effect of Decay Rate on Bed Response for HCB.....	VI-16
6.2.10 Effect of Bed Decay Rate on the Ratio of Bed Contaminants to Concentration on Suspended Solids.....	VI-17
6.2.11 The Effect of Settling Velocity on the Response Time of the Bed.....	VI-19
6.2.12 Comparison of the Predicted Concentration Profile with Measured Data at Port Lambton.....	VI-20
6.2.13 Comparison of the 1986 Predicted and Investigative HCB Concentrations along the Canadian Shoreline in the Vicinity of Dow Chemical.....	VI-21
6.2.14 Sensitivity of Contaminant Loss to Volatilization Parameters...	VI-23
6.2.15 Near Shore and Off Shore WASTOX Cells.....	VI-24
6.2.16 Preliminary Food Chain for Lake St. Clair/St. Clair River.....	VI-26
6.2.17 Predicted and Measured HCB Body Burdens in Adult Sport Fish in Mitchell's Bay (1985).....	VI-32
6.2.18 Predicted and Measured OCS Body Burden in Adult Sport Fish in Mitchell's Bay (1985).....	VI-33
6.2.19 Predicted Distribution of HCB in Adult Sport Fish in Lake St. Clair.....	VI-34
6.2.20 Predicted Distribution of OCS in Adult Sport Fish in Lake St. Clair.....	VI-35
6.2.21 Body Burden of HCB and OCS in the Species of the WASTOX Food Chain for Lake St. Clair (1985).....	VI-36
6.2.22 Predicted Total HCB Concentrations in Water Cells of Lake St. Clair in ng/L for 1985.....	VI-38

## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
6.2.23 Predicted Total OCS Concentrations in Water Cells of Lake St. Clair in ng/L for 1985.....	VI-39
6.2.24 Simplified 4 Level Generic Food Chain.....	VI-40
6.2.25 Effects of $K_{OW}$ , TOC and Suspended Solids on Body Burden in Fish.....	VI-43
6.3.1 Variation of the Surface and Bottom Concentrations at Slightly Buoyant Shore Based Outfalls.....	VI-46
6.5.1 Model Calibration Error Versus Distance From the Load Source..	VI-53
6.5.2 Load Frequency Curve for HCB at the Dow 1st Street Sewer Complex Based on the 1986-1987 Mean Monthly Loads.....	VI-54
6.5.3 Normalized Load Frequency Curve for the Cole Drain for HCB, HCBd, HCE, PERC and CCL4.....	VI-55
6.5.4 Normalized Load Frequency Curve for the Dow 1st Street Sewer Complex for HCB, HCBd, HCE, PERC and CCL4.....	VI-56
6.5.5 Normalized Load Frequency Curve for the Dow 2nd Street Sewer for HCB, HCBd, HCE, PERC and CCL4.....	VI-57
6.5.6 Normalized Load Frequency Curve for the Dow 3rd Street Sewer for HCB, HCBd, HCE, PERC and CCL4.....	VI-58
6.5.7 Normalized Load Frequency Curve for the Dow 4th Street Sewer for HCB, HCBd, HCE, PERC and CCL4.....	VI-59
6.5.8 Flow Frequency Curve for the St. Clair River.....	VI-60
6.5.9 Calibration Error in KETOX.....	VI-61
6.6.1 Cole drain HCB Load Allocation for MZ-30m.....	VI-65
6.6.2 Polysar 72-inch HCB Load Allocation for MZ - 30m.....	VI-66
6.6.3 Dow 1st Street Complex Load Allocation for MZ - 30m.....	VI-70
6.6.4 Dow 4th Street Load Allocation for MZ - 30m.....	VI-71
6.6.5 Predicted and Measured (GLI) HCB in Clams in Lake St. Clair [Sta. 1 South-East; Sta. 2 Mid-East; Sta. 3 South Channel Plume].....	VI-73

## LIST OF FIGURES (Cont'd)

<u>FIGURE</u>	<u>PAGE</u>
6.6.6 Predicted and Measured (GLI) OCS in Clams in Lake St. Clair [Sta. 1 South-East; Sta. 2 Mid-East; Sta. 3 South Channel Plume].....	VI-74
6.6.7 Calibration Error Frequency Curve for Biota Sub-Models.....	VI-75
6.6.8 Body Burden Response Curve for HCB in Adult Sport Fish Near Dow Chemical.....	VI-78
6.6.9 Body Burden Response Curve for HCB in Adult Sport Fish Near Port Lambton.....	VI-79
6.6.10 Body Burden Response Curve for HCB in Adult Sport Fish Mitchell's Bay, Lake St. Clair.....	VI-80
6.6.11 KETOX - Thomann Model for Biota Based Load Allocation for HCB at the Dow 1st Street Sewer Complex.....	VI-82
6.6.12 Comparison of the WASTOX Predicted and MOE Measured Bed Concentrations on Sediments for 1985 Loads.....	VI-88
6.6.13 Calibration Error Frequency Curve for the Sediment System for HCB Based on 1985 Data.....	VI-89
6.6.14 Sediment Contaminant-Load Frequency Curve for HCB at Dow 1st Street Sewer.....	VI-90

## LIST OF APPENDICES

APPENDIX 1	LONG-TERM EFFLUENT MONITORING RESULTS
APPENDIX 2	GC/MS RESULTS FOR CONTAMINANTS MEASURED ON SUSPENDED SOLIDS FROM EFFLUENT STREAMS
APPENDIX 3	EFFLUENT AND AMBIENT SEQUENTIAL SAMPLING RESULTS
APPENDIX 4.1	GC/MS RESULTS FOR CONTAMINANTS MEASURED ON AMBIENT SUSPENDED SOLIDS
APPENDIX 4.2	CONVENTIONAL RESULTS FROM AMBIENT CENTRIFUGATION
APPENDIX 4.3	CONVENTIONAL RESULTS FROM EFFLUENT CENTRIFUGATION
APPENDIX 4.4	SURFICIAL BOTTOM SEDIMENT RESULTS
APPENDIX 5	RESULTS FROM INVESTIGATIVE AMBIENT WATER SAMPLING
APPENDIX 6a	CLAM TISSUE PREPARATION FOR VOLATILES ANALYSIS
APPENDIX 6b	RESULTS OF CLAM TISSUE CONTAMINANT ANALYSIS FOR SELECTED PARAMETERS
APPENDIX 7	KETOX MODELLING USERS GUIDE
APPENDIX 9	LOAD ALLOCATIONS FOR WATER; BIOTA AND SEDIMENTS BY CHEMICAL AND OUTFALL



## 1.0 INTRODUCTION

### 1.1 Overview of the MISA Initiative

Since the June 1986 release of the Ministry of the Environment's (MOE) White Paper, entitled "Municipal-Industrial Strategy for Abatement" (MISA), a comprehensive abatement program has been under development to establish regulations for controlling water pollution at its source.

The White Paper provides the framework for the control of toxic contaminants in industrial and municipal effluents; initially, through a regulatory component to enforce technology-based effluent standards. The minimum pollution control requirement will be based upon implementation of best available technology economically achievable (BATEA).

Development of these controls will be accomplished through the promulgation of two regulations:

- (1) the Effluent Monitoring Regulation, requiring dischargers to measure concentrations and loadings of toxic contaminants in their effluents, as specified in the Ontario Effluent Monitoring Priority Pollutants List (EMPPL); and
- (2) the Limits Regulation, specifying maximum permitted loadings of toxic pollutants for point-source dischargers.

Where necessary, in environmentally sensitive areas, technology-based effluent limits will be compared with site-specific, receiving-water-based effluent limits. The site-specific limits will consider the environmental sensitivity of water bodies, where more stringent limits than those prescribed by BATEA may be required.

### 1.2 Development of Receiving-Water-Based Effluent Limits

To assist in developing standard procedures for the derivation of receiving-water-based effluent limits, the Ministry has evaluated numerous traditional and novel water quality assessment techniques. These

techniques have been applied on a site-specific basis at six "Pilot Sites" throughout Ontario, to determine their suitability in establishing receiving-water-based effluent limits.

The six Pilot Sites were selected to provide a cross-section of industrial/municipal dischargers and receiving-water environments existing in Ontario. The six sites, and the principal dischargers studied, are as follows:

- (1) Kaministiquia River at Thunder Bay (Canadian Pacific Forest Products, formerly Great Lakes Forest Products)
- (2) St. Marys River at Sault Ste. Marie (Algoma Steel)
- (3) St. Clair River at Sarnia (Dow Chemical)
- (4) Grand River at Waterloo (Waterloo Sewage Treatment Plant [STP])
- (5) Lake Ontario at Toronto (Toronto Main STP)
- (6) St. Lawrence River at Cornwall (Several Municipal and Industrial Sources)

As a basis for determining the impacts of toxic contaminants on the aquatic environment, the Pilot Site study teams have relied on Provincial Water Quality Objectives (PWQO's), Guidelines (PWQG's), advisories, as well as water- and biologically-based criteria developed by other government agencies, to determine acceptable conditions.

Water quality "advisories" are values which have been developed to protect aquatic life based on a very limited amount of toxicological information. The Ministry has developed a hierarchical protocol for developing water quality Objectives (PWQOs); Guidelines (PWQGs) and advisories based on a descending level of available chronic and acute toxicity information. The safety factors applied in deriving PWQO, PWQG and advisories may range from 10 to 9,000 depending on the amount of toxicological information available.

To establish and simulate the cause-effect relationships between source and receiver, these studies have built upon classical and newly verified biological and modelling assessment techniques to account for the complex behaviour of some of these toxic compounds.



### 1.3 The St. Clair River MISA Pilot Site Study

This report incorporates specific studies undertaken in the St. Clair River (Figures 1a, b, c) from May 1986 to May 1988 to assess the impacts of discharges from Dow Chemical Canada Inc. (Dow) on the river, both locally and downstream. In order to discriminate the effects of sources at Dow from potential upstream sources, additional sampling occurred at the Cole drain and Polysar Ltd. (Sarnia). As a result, specific impacts from the upstream sewers were also evaluated at a level of detail similar to that applied at Dow.

Scientific investigations have included sampling at selected outfalls in the area, coupled with water and sediment quality sampling and biomonitoring of the entire St. Clair River.

Data collected from these studies have been used for calibrating and subsequently verifying state-of-the-art predictive fate and transport models. These models were applied to determine the toxic contaminant distribution in the St. Clair River.

The studies were designed to evaluate the impacts of chemicals of concern discharged to the St. Clair River, in order to fulfill the two primary goals of this investigation:

- (1) Develop site-specific effluent requirements for hazardous and conventional pollutants from designated discharges on the St. Clair River, based on receiving-water impact assessments.
- (2) Develop and document, for application to other comparable discharger and receiving-water situations in the Province, an acceptable set of receiving-water assessment techniques and procedures.



## 2.0 SITE DESCRIPTION

### 2.1 Description of the Pilot Site Study Area

The pilot site study area focused primarily on a 2.4 km stretch of the St. Clair River bounded by the Cole drain to the north and the Dow-Suncor property line to the south (Figure 2.1). Studies also addressed environmental effects further afield and as such, additional sampling was conducted along the entire river length. The physical characteristics of the area can be described on a Regional basis.

#### 2.1.1 Hydrology of the St. Clair River

The St. Clair River is a 64 km (40 miles) long international connecting channel flowing south from Lake Huron into Lake St. Clair (Figure 2.2). The river has a swift current exceeding 3 m/sec. in some stretches with an average discharge rate of 6366 m<sup>3</sup>/sec. The drop in elevation is approximately 2.5m along its entire length. Maximum depths range from 7m to 9m. There are shallow shelves along the nearshore areas with a steep drop-off to a deep centre channel. The St. Clair River contributes ninety-eight percent of the water to the Lake St. Clair basin. The remaining 2% is contributed by other lake tributaries.

#### 2.1.2 Area Land and Water Uses

The St. Clair River has contributed significantly to the economy of the Great Lakes Basin. There are six distinct uses of the St. Clair River: industrial and domestic water supplies; effluent disposal; commercial navigation; sport fisheries including yellow perch and walleye; wildlife habitat; and general recreation. The "Chemical Valley" at Sarnia refers to the presence of numerous petroleum refineries and petrochemical plants near the river, south of the City's business core. There are approximately 22 direct outfalls

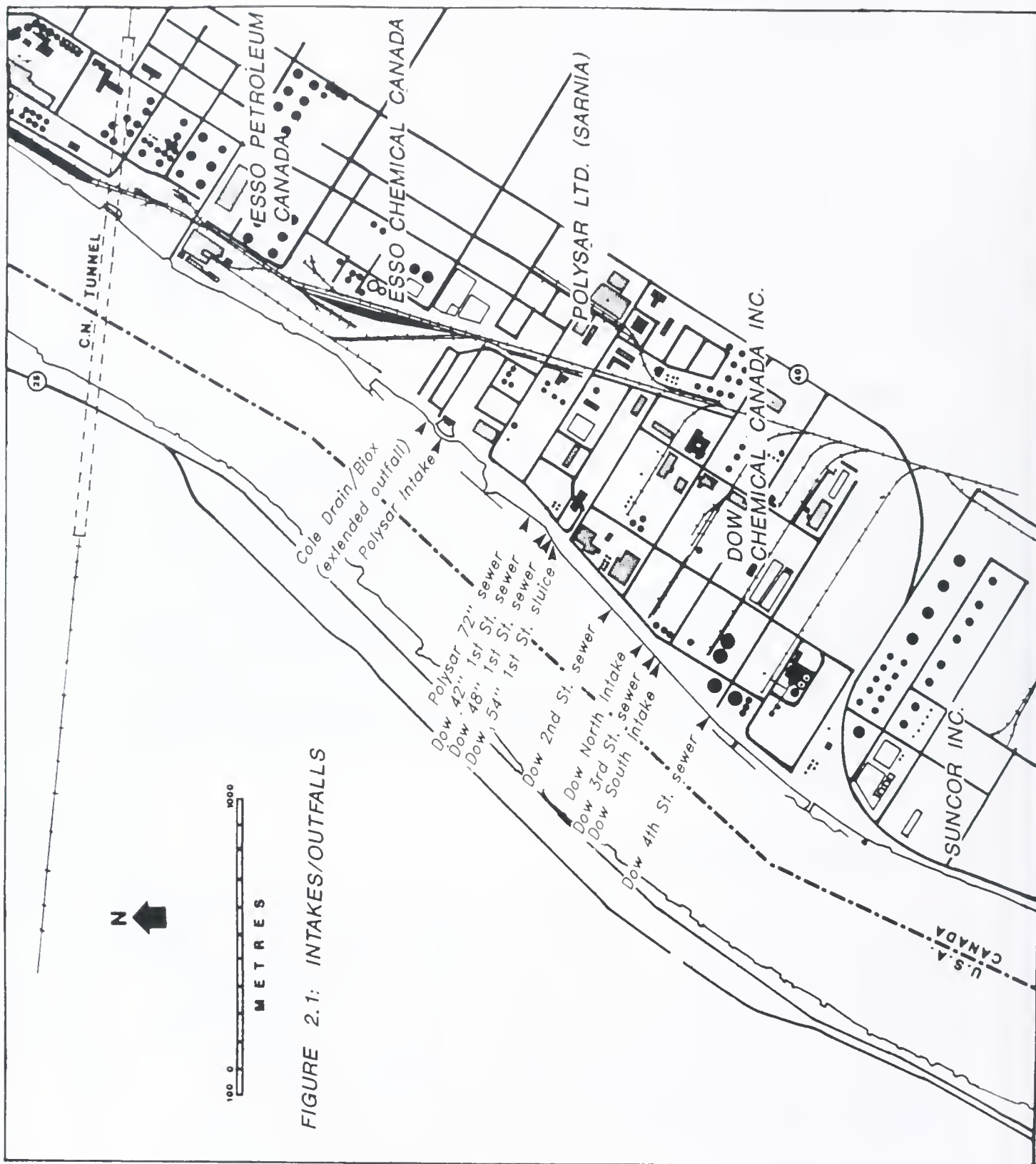


FIGURE 2.1: INTAKES/OUTFALLS

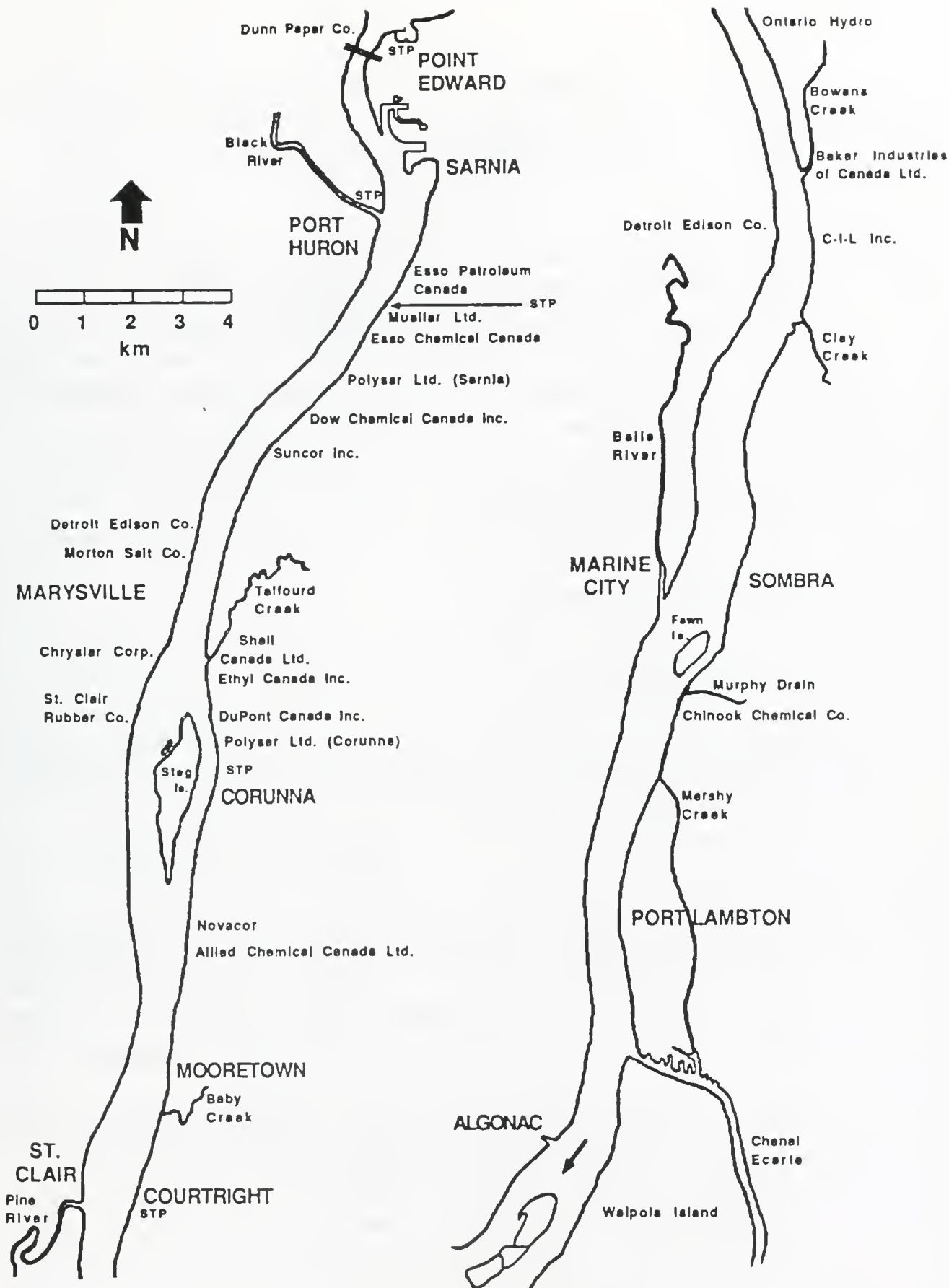


FIGURE 2.2: THE ST. CLAIR RIVER

including storm sewers along the St. Clair river within the 2.4 km stretch from the Cole drain to Suncor. Those outfalls selected for sampling at Dow and Polysar are identified in Figure 2.1. These plants produce a variety of petrochemicals and petroleum products.

The river is heavily used for international shipping. The shipping channel has been maintained by dredging since the 1890's. Channel dredging has altered river levels and discharge to Lake St. Clair. Fishing and recreational boating are popular past times enjoyed on the River, and there are many shoreline parks and marinas. Shoreline development is concentrated at the north end near Lake Huron in cross-channel cities of Port Huron, Michigan and Sarnia, Ontario. These cities have populations of 33,367 and 55,576 respectively. Numerous other population centres dot the river's shoreline. Algonac, Michigan and Port Lambton, Ontario are the centres of development at the southern end of the river.

#### 2.1.3 Geology and Soils

The St. Clair River is in an area of consolidated sedimentary rocks of Precambrian and Paleozoic age overlain by a thin layer of fine clay, glacial deposits. Consolidated rocks include sandstone, shale, limestone, and dolomite. These rocks are part of the Michigan structural basin in which all beds dip toward a common centre. In the St. Clair River area, on the southeastern rim of the basin, the rocks dip to the northwest. Unconsolidated deposits consist of glacial till and glaciolacustrine deposits. These deposits are the result of continental glaciation and subsequent high water levels of the Great Lakes.

This clay layer, on the order of 30m in depth, is considered suitable for waste containment in that it produces low solute transport rates by advection. This is due to low hydraulic conductivity and long transport times. Similarly, this type of overburden would not promote rapid transport of land-based spills to the St. Clair River from production and handling sites (GTC 1986).



Bedrock subcropping beneath the St. Clair River is of Devonian-Mississippian age. These rocks include the Port Lambton and Kettle Point formations consisting mainly of shale.

Bedrock topography slopes gently westward toward the St. Clair River. The bedrock surface is dissected by erosional valleys that generally trend east-west. There is no surface expression of these valleys because they are filled with glacial deposits.

Surficial features of glacial deposits include till plains, moraines, lakebeds, and beach ridges. Moraines and beach ridges generally trend parallel to present day shorelines and are the result of the Huron ice lobe of Pleistocene glaciation and numerous high water levels of the Great Lakes during the Glacial Epoch.

Glacial deposits range in thickness from 30m to about 76m. Till and glaciolacustrine deposits are usually well sorted sands and gravels. Glaciofluvial or outwash deposits are absent at the surface in the area. Sand and gravel deposits are not significant and do not occur to any great depth. They are most common at the interface of glacial deposits and bedrock, and where found, are usually discontinuous.

## 2.2 Description of Point Sources

Point sources are defined as a source of pollution that is distinct and identifiable, such as an outfall pipe from an industrial or municipal plant.

### 2.2.1 Dow Chemical Canada Inc., Sarnia Division

In 1942, Dow developed a highly diversified petrochemical complex in order to produce synthetic rubber for the war effort. The Sarnia plant is now made up of 13 individual plants producing the following products:

Vinyl Chloride Monomer  
Trichloroethane  
Carbon Tetrachloride  
Tetrachloroethylene  
Propylene oxide and Polypropylene Glycols  
Polyglycols  
Chlorine and Caustic Soda  
Ethylbenzene  
Polystyrene  
Styrene Monomer  
Ethylene Glycols  
Anhydrous Hydrochloric Acid  
Vinyl Ester Epoxy Resins  
Latex  
High and Low Density Polyethylene

Dow Chemical, Sarnia has nine separate direct and indirect discharges to the St. Clair River and two water intake pumphouses, both of which are located downstream of the first street sewer complex and the second street sewer (Figure 2.1). The plant water intake is typically 730,000 m<sup>3</sup>/day. Treated leachate from the Dow Scott Road landfill site (contactor effluent) is the only indirect discharge from Dow which enters the St. Clair River through the Cole drain.

(i) First Street 42-inch Sewer

The First Street 42-inch sewer presently discharges once through cooling water from the following areas: the vinyl chloride/trichloroethane plant, the solvents area (carbon tetrachloride and perchlorethylene) and the propylene oxide plant. Stormwater runoff (non-process area) from the vinyl chloride/trichloroethane and propylene oxide plants also discharges to this sewer. Prior to November 1986 process water and contaminated stormwater from the vinyl chloride/trichloroethane plant also discharged to this sewer. These effluents have now been directed to the Block 90 pond for spill



containment. The Block 90 pond is an open retention pond which discharges to the Fourth Street sewer.

(ii) First Street 48-inch Sewer

The 48-inch sewer receives once through cooling water only, and is above grade, thus precluding contamination by surface groundwater infiltration. The cooling water originates with the vinyl chloride/trichloroethane and solvents plants.

(iii) First Street 30-inch Acid Tile

The 30-inch acid tile was permanently sealed off in June, 1986 and the streams which discharged to it diverted elsewhere (1st Street 42-inch sewer initially, now to Block 90 pond).

(iv) First Street 54-inch Sluice Sewer

The First Street 54-inch sluice sewer discharges once through cooling water from the propylene oxide, caustic, and chlorine II plants as well as runoff from the chlor-alkali plant. In addition, process water from one of the two thermal oxidizers on site discharges to this sewer (scrubber water). Prior to August 1986 process water and contaminated runoff from the solvents plant was also discharging to this sewer. These streams have now been diverted to the Block 90 pond as a spill containment measure.

The 54-inch sluice was also the route of discharge of the 1985 perchloroethylene spill, which originated at a loading area near the solvent's plant. A valve on a spill containment catch basin tributary to the sluice, was seized in the open position allowing the pure solvent to escape to the river (an estimated 11,000 litres of a total spill of 42,300 litres reached the river - DOE/MOE 1986).

(v) Second Street Sewer

The Second Street sewer receives once through cooling water and stormwater runoff from the polystyrene and propylene oxide derivatives plants. Polystyrene runoff passes through a bead trap prior to discharge. Non-sanitary discharge from Dow's analytical laboratory also discharges to this sewer.

(vi) Third Street Sewer

The Third Street sewer discharges process water, once through cooling water and stormwater runoff originating with the styrene, high density polyethylene (HDPE) and latex plants. The research and development building also discharges to this sewer.

The steam stripper at the styrene unit treats process wastewater and contaminated storm runoff prior to discharge to a cross link between the Third and Fourth Street sewers. Styrene plant process water therefore, discharges to both of these sewers. High density polyethylene and latex plants process waters are also steam stripped prior to discharge to the Third Street sewer.

(vii) Fourth Street Sewer

The Fourth Street sewer also discharges a mix of process, once through cooling and stormwater to the river. The low density polyethylene and chlor-alkali plants discharge once through cooling water and storm runoff only. The tank car washing facility discharges washwater from polystyrene bead tank cars only, to the Fourth Street sewers. Other washwaters are sent to the originating units for recovery of product, with the exception of chlorine and caustic washes which discharge to the Block 90 pond. The Styrene plant process water and the Treatment plant secondary clarifier effluent also discharge to the Fourth Street sewer. The biological oxidation treatment plant treats wastewater

from the propylene oxide and propylene oxide derivatives plants, the latex, styrene, chlor-alkali and HDPE plants, as well as contaminated washwater and storm runoff from a number of locations on site.

The Block 90 pond receives wastewater from the solvents and vinyl chloride plants. It may also receive process water from the First Street caustic and chlorine II plants (normally recycled), water from the recovery wells along the waterfront and the tank car wash discharge. The solvents plant wastewater is made up of stripper bottoms and the vinyl chloride/trichloroethane wastewater originates with thermal oxidizer scrubber discharge, contaminated runoff and pH-adjusted process water.

Finally, filter backwash from the treatment of boiler feed water, once through cooling water from the epoxy plant and runoff from the epoxy plant discharge to Fourth Street. However, the epoxy plant storm runoff may be discharged to the biox if contaminated (tested prior to discharge).

#### 2.2.2 Polysar Limited, Sarnia

Polysar was established in 1942 as the crown corporation Polymer, to produce synthetic rubber in the war effort. Polysar now operates plants in Sarnia and Corunna. For purposes of this investigation, effluent monitoring at Polysar was restricted to the Sarnia plant only, in order to determine the significance of sources upstream of Dow Chemical. A total of 12 sewers (including 4 storm sewers) discharge directly to the St. Clair River from Polysar in Sarnia. The following descriptions are limited to the principle sewers which discharge process and/or cooling water.

##### (i) Biox Unit

The biological treatment plant came on-line in 1983. Initially, process wastewater from all production units except the new butyl

rubber plant, the new styrene plant and the "stereo" unit (polybutadiene rubber) was pre-treated for solids and oil removal as well as pH, depending on the waste stream, before discharging to the biox. After treatment as necessary, the three streams excluded above are treated at the source in the production unit before discharging directly to the 66-inch sewer. A fourth process stream discharges to the 72-inch sewer from the stereo rubber unit. Currently, only the butyl rubber plant is discharged to the 66-inch sewer. The remaining plants undergo treatment and are discharged to the biox.

Most of the process wastewater discharges to a pre-aeration equalization tank since the process unit effluents can be highly variable. The equalized wastewater combines with plant wastewater and waste from Akzo Chemicals Ltd., treated under contract by Polysar. The Certificate of Approval for the biox unit allows Polysar to accept outside wastes with certain characteristics. However, the approval of the local Ministry of the Environment office is required for each waste stream. Outside wastes containing PCBs, pesticides, chlorinated solvents, cyanides or metal finishing solutions are not accepted.

The combined waste stream passes through one or more of four aeration tanks before discharging to the clarifiers (2 in parallel). The biox unit's final effluent discharges to the Cole drain near the bank of the St. Clair River and the combined biox/drain stream discharges via a submerged diffuser 68 metres into the St. Clair River.

(ii) 54-inch Sewer

The 54-inch sewer is a shore-based discharge which conveys once through cooling water, stormwater and boiler blowdown (from the steam plant) to the St. Clair River. Boiler blowdown passes through an API separator for solids removal. The average flow of this sewer is  $100 \times 10^3 \text{ m}^3/\text{day}$ .

### (iii) 66-inch Sewer

The 66-inch sewer is shore-based and discharges once through cooling water, stormwater and process wastewater to the St. Clair River. Rubber containing streams from the newer synthetic butyl rubber plant are treated through a series of API type separators followed by dissolved air flotation for rubber crumb recovery. Oil and hydrocarbon streams pass through oily water separators. The two treated streams, along with cooling tower blowdown combine and discharge to the 66-inch sewer.

Contaminated wastewater from the new styrene unit has oil and other hydrocarbons skimmed off prior to discharging to a stripping tower for total organic carbon (TOC) removal, followed by ozonation to destroy phenolics. The pH can be adjusted and the effluent clarified if necessary. The treated wastewater formerly discharged to the 66-inch sewer, but now enters the biox unit.

Oil and hydrocarbon contaminated streams from the production of synthetic polybutadiene rubber formerly discharged to the 66-inch sewer via the stereo API separator; however, it now also enters the biox unit. The major contaminant in this wastewater is benzene with the major benzene contaminated streams passing through a steam stripping tower before discharging to the biox.

### (iv) 72-inch Sewer

The 72-inch sewer receives once through cooling water, stormwater and process wastewater. The stereo unit finishing wastewater passes through a separator to remove polymer solids prior to discharge. The 72-inch sewer is a shore-based discharge.

## 2.2.3 The Cole Drain and Area Landfills

### 2.2.3.1 The Cole Drain

The Cole drain (Figure 2.1) is an open ditch system servicing an area south of Sarnia's residential and business core. The drainage system

is bounded approximately by the CNR railway track south of Confederation Street on the north, Modeland Road on the east, Churchill Road on the south and the St. Clair River on the west. It receives stormwater runoff from undeveloped and developed land, waste disposal and product storage areas, treated and untreated runoff and industrial process effluent and cooling water. In terms of direct discharges to the St. Clair River, the ditch/drain is considered an industrial point source, and is a major source of organic contaminants to the river.

There are several inputs to the Cole drain including Esso Chemical (stormwater), Cabot Carbon, Fiberglas and Polysar (stormwater). Cabot Carbon manufactures carbon black from liquid feedstock and natural gas. Cooling tower blowdown, laboratory wastes, boiler blowdown, equipment washwater and surface runoff discharge to the Cole drain. A wastewater treatment system removes carbon black and oil from the effluent. Fiberglas manufactures glass fiber insulation with phenolic and urea resins incorporated into the product. Process water passes through a solids separator before combining with cooling water and discharging to the drain. The process water contains small glass beads but would not normally be contaminated by resins unless a spill occurred within the plant.

The final section of the Cole drain is lined with concrete and flows through Akzo Chemicals Ltd., BASF Canada Inc. and Polysar property. It receives mainly cooling water and stormwater runoff, as well as laboratory wastewater. The Polysar biological oxidation treatment plant discharges to the drain just prior to it going below grade and discharging via a submerged outfall. BASF discharges 2 cooling water/stormwater streams to the Cole Drain.

Sediments of the St. Clair river were highly contaminated by tars discharging from the Cole Drain prior to 1980 (MOE 1979). In 1984, the entire Cole drain from Scott Road to Polysar was dredged and the contaminated material was disposed of at the Scott Road landfill.



#### 2.2.3.2 The Scott Road Ditch

The first major upstream area of influence on the Cole drain is the Scott Road ditch which serves as an industrial and municipal waste disposal area. Waste disposal sites along Scott Road are owned by Polysar Limited (Polysar), Dow Chemical of Canada Ltd. (Dow), Fiberglas Canada, Imperial Oil (Esso Refinery and Chemical Plant), as well as the City of Sarnia (sewage sludge disposal lagoons). The Scott Road ditch runs along the western edge of the industrial waste disposal area and receives treated leachate and storm runoff before joining the Cole drain, which up to this point, contains mostly undeveloped area runoff, as well as storm water runoff from the CN rail yard and cooling tower blowdown. An open ditch exists along Scott Road from Churchill Road to Imperial Avenue. There, a submerged tile conveys runoff to the Cole drain. The Imperial Oil waste disposal site located north of Churchill Road is capped and surface runoff discharges to the ditch.

Partek Insulation Limited (formerly Holmes Insulation) is located on Scott Road and discharges cooling water only to the Scott Road ditch opposite the Imperial Oil disposal site. Pipe insulation, insulating block, board, felts, blankets and cements, bulk and blowing wool are manufactured on site. Process water is entirely recycled.

Upstream of the point at which it joins the Scott Road ditch, the Cole drain receives surface runoff from the areas of Plank and Indian Roads and the MacGregor Side Road. The CN rail yard runoff passes through an oil-water separator and also discharges to this part of the ditch. Dome Petroleum discharges cooling tower blowdown and storm runoff to the ditch upstream of the CN yard.

#### 2.2.3.3 The Fiberglas Canada Disposal Site

The Fiberglas Canada disposal site, containing buried waste fiberglass, is north of Imperial's waste disposal site. Bonding resins and dyes were at one time leaching out of this site. The leachate was collected and pumped into a holding lagoon where it was



treated with calcium chloride before being discharged to the Scott Road tile drain. The site was subsequently capped and a leachate collection system was installed. Leachate is now shipped off the property for treatment and disposal.

#### 2.2.3.4 The Dow Chemical Scott Road Landfill

The Dow Chemical Scott Road landfill site is located directly north of Fiberglas. A reinforced steel barrier composed of interlocking steel piling retains all leachate within the disposal site (pilings down to unfractured clay bed at 3-4 metres). The leachate is collected in a perimeter pond at the north edge of the property and pumped through carbon filters before being discharged to the Scott Road ditch. This discharge is intermittent and depends on precipitation and the level of leachate in the pond. Leachate from the Dow disposal site, prior to the installation of the carbon filters, contaminated the sediments of the Scott Road ditch and the Township ditch, with hexachlorobenzene (HCB) and hexachlorobutadiene (HCBd). The Scott Road ditch was subsequently excavated and replaced with a submerged corrugated steel sewer. In 1983/84 Dow dredged the affected section of the Cole drain and disposed of the sediment at the Scott Road landfill site.

#### 2.2.3.5 The Polysar Disposal Site

The Polysar disposal site is located south and east of the Dow site. The leachate is aerated and then directed to a fly ash pond which acts as a filter/adsorbant. Storm runoff and treated leachate from the fly ash pond are piped to the Polysar biological treatment plant.

### 2.3 Description of Non-Point Sources

An indirect, yet potentially significant source of contaminants to the St. Clair River arises from urban and rural runoff and drainage of poorly defined origin. Non-point sources discharge to the river via combined sewer overflows, storm water discharges, overland flow, groundwater intrusion and tributary inputs.

An example of a non-point source to the St. Clair River is agricultural pesticide run-off. Some of these pesticides have the potential of being environmentally hazardous. While documentation of the use of these agricultural pesticides is complete, the fate of these chemicals in the environment is unclear.

Further non-point source contamination may arise through the movement of shallow groundwater containing material spilled on land in the vicinity of process plants and/or product handling areas.

### 2.3.1 Combined Sewer Overflows

Combined sewer overflows (CSOs) occur in older municipal sewer systems, constructed prior to the 1960's, when sewers were designed to convey both sanitary sewage and storm water runoff. During periods of wet weather, or in systems with dry weather flows now exceeding interceptor or treatment plant capacity, untreated sewage can discharge directly to the receiving water.

Treatment plant by-passes at the water pollution control plant (WPCP) or sewage treatment plant (STP) can occur during dry weather periods in systems when the total sanitary discharge into the municipal sewer system exceeds treatment plant capacity, as well as during wet weather in municipalities serviced with combined sewers.

Sarnia is a major urban centre which has 4 wet weather combined sewer overflows and 11 storm water outfalls. Two of the combined sewer overflows and 3 of the storm sewers service the "Chemical Valley" and are sources of ammonia, phosphorus, oil and grease, zinc and mercury (UGLCCS 1989).



### 3.0 STUDY OUTLINE

#### 3.1 Study Overview

It will become apparent in the following sections that the St. Clair River Ecosystem is both dynamic and complex. In order to define existing aquatic environmental conditions and to allow for the assessment of future trends, after the initiation and enforcement of new MISA regulations, numerous assessment methods were evaluated.

Sampling protocols and analytical techniques used during the field and laboratory exercises were examined. Technique assessment considered the appropriateness of the methods for future monitoring purposes at other locations throughout the province.

Techniques under development which will enable the derivation of water quality-based effluent limits are chemical specific. As such, an abbreviated list of the parameters of concern was developed by the pilot site team.

Parameters were selected due to known emissions to the St. Clair River and serve to "finger print" historical and/or process related contamination from the Dow Chemical site. These chemicals have demonstrated adverse effects on the environment and are therefore listed in the MISA Effluent Monitoring Priority Pollutants List (EMPPL 1987).

The list includes:

- 1) Hexachlorobenzene (HCB)
- 2) Hexachlorobutadiene (HCBd)
- 3) Hexachloroethane (HCE)
- 4) Octachlorostyrene (OCS)
- 5) 2,4,5 - Trichlorotoluene (2,4,5-TCT)
- 6) Carbon Tetrachloride (CCL<sub>4</sub>)
- 7) Tetrachloroethylene (Perc)
- 8) Mercury (Hg)

Provincial Water Quality Objectives/Guidelines (PWQO/PWQG) will ultimately be developed for all EMPPL compounds. As well, development of sediment quality guidelines and aquatic life tissue residue guidelines for these and other compounds is currently underway.

Once suitable guidelines are established, it is possible using existing fate and transport models (i.e. mathematical models), to link water quality conditions to point source discharges. This enables the determination of the maximum allowable level of contaminant discharges to a receiving water body. The use of fate and transport models establishes a link between the sediment, water column and aquatic biota. These models are continually being refined, with particular attention to improvements in the estimation of contaminant transfer through the food-web.

### 3.2 Description of Monitoring Strategies

#### 3.2.1 Sediment/Benthos Monitoring and Evaluation

Four sediment/benthic study components evaluated the temporal and spatial trends of contaminant impact within the St. Clair River, as expressed by overt reactions within the benthic environment. Bulk sediment chemistry, contaminant levels in the benthos, sediment toxicity and benthic community structure were critically assessed to determine the health of the benthic environment as well as for their use in fate and transport models.

#### 3.2.2 Biota Monitoring and Evaluation

Eight distinct investigations using biomonitors were conducted. The purpose of each exposure was to assess a specific type of biota for its suitability as an indicator organism and to evaluate its utility in contaminant fate and transport modelling. The following provides a brief description of each of these investigations:

- 1) Phytoplankton monitoring for biomass as well as contaminant exposure (including seston);
- 2) Bacterial slime occurrence and density was assessed;
- 3) Heterotrophic bacteria were surveyed to document numbers present in the surficial sediments and bottom waters. An analysis of their abundance provides information relevant to the extent of biodegradable pollution;
- 4) Macrophyte biomass and contaminant load were surveyed in order to assess their importance as bioaccumulators of contaminants;
- 5) Cladophora samples were collected in order to assess their potential for bioaccumulation of contaminants. Cladophora is a predominant attached green alga of the St. Clair River;
- 6) Indigenous forage fish were evaluated for their potential as biomonitors. Young-of-the-year (Juvenile) spottail shiners (Notropis hudsonius) and emerald shiners (Notropis atherinoides) were used for this purpose;
- 7) Sportfish were analysed for contaminant burdens in the edible portion. Sportfish are important both as potential biomonitors for their impact to wildlife and human health;
- 8) Introduced freshwater clams Elliptio complanata were exposed in specific, confined areas as biomonitors.

### 3.2.3 Effluent Monitoring and Evaluation

Two principle methods were used to assess variability in effluent quality from point sources at Dow and Polysar. The long-term effluent monitoring program provided insight into long-term variability, trends subsequent to remedial measures and an accurate estimate of

contaminant loadings to the St. Clair River. The sequential monitoring study was performed to assess nearfield cause/effect relationships between the receiver and specific outfalls and to provide data on short-term variability in effluent quality. Both components were critical to the calibration and verification of contaminant fate and transport models.

#### 3.2.4 Water Column Monitoring and Evaluation

The condition of the St. Clair River was further evaluated by means of a number of water quality monitoring studies. These included surface and bottom water sampling at 43 stations throughout the St. Clair River as part of the Investigative Water Quality Study. Further assessments included centrifugation of surface and bottom waters to quantify partitioning of contaminants between the aqueous (dissolved) and solid particulate phases. In addition, concurrent water and effluent sampling was undertaken as part of the Sequential sampling described above.

The data collected from these various "environmental compartments" were used for the calibration and validation of fate and transport models. These models provide us with a tool to better assess and account for the "total" impact of a contaminant on the aquatic ecosystem. This is accomplished through the evaluation and integration of the transport and partitioning of the contaminant through the "food web" from the water column and sediments.

Fate and transport models thereby establish a link between the source of a contaminant and a trophic level of interest (for example sportfish). These models have been used in the determination of acceptable loading rates, waste load allocation limits and the development of effluent requirements, based on water quality impacts on a site-specific basis. This will permit the implementation of controls on the basis of impact on the aquatic environment.



The incorporation of data, for environmentally relevant contaminants, obtained from the various compartments (sediment, water, biota and atmosphere) into fate and transport models brings us to a new era of whole ecosystem impact assessment. The use of contaminant concentrations in the water column to assess aquatic environmental fate and effects, will no longer be used in isolation; but, in concert with biological and sediment data.



## 4.0 METHODOLOGY AND DISCUSSION OF RESULTS FOR SPECIFIC MEDIA

### 4.1 Effluent Monitoring

#### 4.1.1 Long-Term Effluent Monitoring

##### (a) Introduction and Purpose

In order to document industrial effluent quality, a long-term (May 1986 - March 1987) outfall monitoring program was implemented as part of the MISA pilot site activities. This sampling was initiated to identify the range of concentrations of selected compounds and to provide a measure of effluent variability with time.

It was anticipated that these results would provide evidence of the effect of remedial measures implemented at Dow Chemical since late 1985. Further, this data coupled with discharge volumes would enable the calculation of accurate contaminant loadings.

##### (b) Methods

Staff from the Southwest Region of the Ministry of the Environment obtained samples randomly on a twice weekly schedule commencing May 15th 1986. Six outfalls at Dow Chemical (1st St. (42-inch, 48-inch, 54-inch); 2nd St., 3rd St., and 4th St.) and 3 at Polysar (72-inch; Cole drain; and Biox) were sampled to the end of March 1987. Sampling at the Dow 2nd St. outfall did not commence until June 27, 1986.

A custom designed basket sampler permitted two bottles to be filled simultaneously at approximately mid-depth in each effluent stream. Parameters tested included chlorinated aromatics, volatiles, mercury, cadmium, lead, nutrients and conventionals. Table 4.1.1 provides a list of organic parameters tested. Particular care was taken to ensure that all air was excluded from the 8 oz. volatile sample (i.e. no headspace).

TABLE 4.1.1: EFFLUENT/WATER QUALITY PARAMETER LIST

Volatile Organic Compounds:		Media	Chlorinated Aromatics/OC Pesticides:		Media
1,1-Dichloroethylene		B	Hexachloroethane		B
Dichloromethane		B	1,3,5-Trichlorobenzene		B
1,2-Dichloroethylene		B	1,2,4-Trichlorobenzene		B
1,1-Dichloroethane		B	Hexachlorobutadiene		B
Chloroform		B	1,2,3-Trichlorobenzene		B
1,1,1-Trichloroethane		B	2,4,5-Trichlorotoluene		B
1,2-Dichloroethane		B	2,3,6-Trichlorotoluene		B
Carbon tetrachloride		B	1,2,3,5-Tetrachlorobenzene		B
Benzene		B	1,2,4,5-Tetrachlorobenzene		B
1,2-Dichloropropane		B	2,6,8-Trichlorotoluene		B
Trichloroethylene		B	1,2,3,4-Tetrachlorobenzene		B
Dichlorobromomethane		B	Pentachlorobenzene		B
Toluene		B	PCB, Total		B
1,1,2-Trichloroethane		B	Hexachlorobenzene		B
Chlorodibromomethane		B	Heptachlor		W
Tetrachloroethylene		B	Aldrin		W
Chlorobenzene		B	p'p'-DDE		W
Trifluorochlorotoluene		B	Mirex		W
Total Trihalomethanes		B	$\alpha$ -BHC (Hexachlorocyclohexane)		W
Ethylbenzene		B	$\beta$ -BHC (Hexachlorocyclohexane)		W
p-Xylene		B	$\gamma$ -BHC (Hexachlorocyclohexane)		W
m-Xylene		B	A-Chlordane		W
Bromoform		B	G-Chlordane		W
o-Xylene		B	Oxychlordane		W
1,1,2,2-Tetrachloroethane		B	o'p'-DDT		W
1,4-Dichlorobenzene		B	p'p'-DDD		W
			p'p'-DDT		W
Detection limit: 1 $\mu$ g/L			DMDT Methoxychlor		W
			Heptachlorepoide		W
			Endosulfan I		W
			Dieldrin		W
			Endrin		W
			Endosulfan II		W
			Endosulfan Sulphate		W
			Octachlorostyrene		W
			Toxaphene		W
			Detection Limit: 1 ng/L		
			Major Ions:		
			pH		B
			Calcium		B
			Magnesium		B
			Sodium		B
			Potassium		B
			Chloride		B
			Fluoride		B
			Sulphate		B
			Silicates		B
			Carbonate		B
			Phosphate		B
Water Chemistry Parameters:					
Dissolved organic carbon	(0.1)	B			
Dissolved inorganic carbon	(0.3)	B			
Chloride	(0.1)	B			
Conductivity	(0)	B			
Suspended solids	(0.5)	B			
Alkalinity	(0.7)	B			
Hardness	(2)	B			
Total phosphorus	(0.001)	B			
Ammonia	(0.007)	B			
Kjeldahl nitrogen	(0.1)	B			
Nitrate	(0.0018)	B			
Nitrate	(0.02)	B			
Mercury	(0.01 $\mu$ g/L)	B			
Lead	(0.003)	B			
Cadmium	(0.0003)	B			
Typical Detection Limits:	(mg/L)				

Legend: W - measured in water only  
 B - measured in water and effluent

Sampling protocols were in accordance with standard MOE procedures (MOE 1985).

Samples were shipped the same day or kept refrigerated and shipped the following day via courier overnight delivery to the Ministry's laboratory in Rexdale, Ontario.

Analysis for each parameter was conducted as described in "Outlines of Analytical Methods" (MOE 1981a).

(c) Results and Discussion

(i) Rationale for Selection of Point Sources

Outfalls were selected to enable documentation of all significant point sources at Dow Chemical. In addition, several important outfalls from Polysar were sampled in order to document their relative contribution to the overall contaminant load. The Polysar 66-inch sewer was not sampled, as it was determined to no longer be a significant source of benzene following a process modification (MOE/DOE 1988).

As a result of modifications in effluent stream configurations at Dow Chemical since November 1985, it is not entirely appropriate to compare results from individual outfalls both pre-and post-modifications. A review of information will be conducted with consideration to assessing additive or facility loadings where necessary.

Due to the nature of processes which occur at Dow, a number of unique contaminants are discharged to the St. Clair River. These process-related contaminants have been shown to occur in consistent ratios with other contaminants and this ratio enables the source to be determined through a comparison of ambient samples with effluent concentrations (DOE/MOE 1986). By selecting these specific chemicals, a useful "finger-print" of the effect on the St. Clair River can be obtained.

It is important to note that the Cole drain which discharges by-way-of a 68m extended, submerged outfall at the Polysar northern property line, receives waste-,cooling- and stormwater from Polysar, the biological oxidation unit (biox), cooling- and stormwater from Partek Insulation, Cabot Carbon, BASF Canada, Akzo Chemicals and Esso Chemical, as well as treated and untreated leachate from upstream landfills.

These landfills include the Polysar flyash pond as well as the Dow Scott Road landfill site which discharge treated and untreated leachate and runoff to the Scott Road ditch and ultimately the Cole drain. As such, discharges from the Cole drain reflect current inputs from Polysar, Akzo, BASF, Partek, Cabot Carbon and Esso Chemical as well as industries which supply wastes for treatment by means of biological oxidation. While Polysar received outside waste during the study period, they no longer do so. Further, inputs from various landfills represent potential contamination from material deposited in the past. For example, The Dow Scott Road landfill received waste during the period 1950-1986.

Sewer effluent sampling occurred on a two-times per week basis at nine sampling points. Initially sampling was conducted regularly on Tuesdays and Thursdays. Following the 1st month, sampling occurred on a random basis during the Monday to Friday work week.

From December 1986 to March 1987 sampling frequency was curtailed due to inclement weather and time constraints. During this period 3-6 samples were collected per month. At each outfall, between 42 and 74 samples were collected in they May 1986-March 1987 period, yielding approximately 600 analyses for each parameter.

For details of the Dow sewer configuration at the time of sampling, the reader is referred to Section 2.2.1.

### Changes to the Dow sewer configuration:

Runoff from the vinyl chloride plant is diverted to a containment pond prior to discharge to the St. Clair River, thereby preventing spills in the area from reaching the River. This change was partially completed in March 1988 prior to a work stoppage and is now completed.

An anticipated benefit from the isolation of runoff water will be the ability to determine the significance of this source relative to cooling water and to implement further abatement measures such as improved recycling of runoff.

### (ii) Historical Inputs

The 1986 St. Clair River Pollution Investigation (Sarnia Area) report prepared jointly by Environment Canada and the Ontario Ministry of the Environment documented the effects of a spill of tetrachloroethylene (Perc) from Dow Chemical which occurred during August 1985 (DOE/MOE 1986).

Information on effluent and receiving water conditions reported in that document included data from the time of publication (January 1986) to several years earlier.

Ambient conditions measured 100m downstream from the 1st St. sewer complex during 1984 revealed levels of chlorinated compounds such as hexachloroethane (HCE), hexachlorobutadiene (HCBD) and hexachlorobenzene (HCB) averaging 0.2-0.5 ug/L (ppb)(DOE/MOE 1986). An empirical estimate of effluent concentrations based on the above ambient conditions and a dilution factor of 25:1 expected to occur at this location (P. Nettleton, MOE pers. comm. 1988) yields predicted effluent concentrations in the 5.0-12.5 ppb range from the 1st St. complex. Based on this information and 1985 discharge rates (DOE/MOE 1986), loadings from the 4 sewers which discharged at the 1st St. complex during 1984 would have been on the order of 0.8 to 2.0 kg/day.



These results were confirmed by observed effluent concentrations for each compound (DOE/MOE 1986) which ranged from 1.4 to 2.9 ppb during November 1985 and may in fact reflect somewhat improved conditions. Mean concentrations for the above parameters (HCE, HCBd, HCB), measured during 1986/87 from the Dow 42-inch sewer were 0.1 to 1.3 ppb reflecting further improvements. Based on a dilution factor of 25:1, approximately 100m downstream of 1st St. complex, predicted ambient concentrations (0.2 - 0.5 ppb) fall within the observed range.

### Historical Loadings and Remedial Measures

Dow Chemical point source loadings were estimated in the November 1985 point source survey (DOE/MOE 1986). In most instances, based on initial findings of the MISA pilot site investigation preliminary report (MOE 1987), significant reductions were noted between November 1985 and September 1986.

A number of recommendations were proposed in the January 1986 spill investigation report (DOE/MOE 1986) for identifying and eliminating point sources. In response to these recommendations, government and industry have implemented a number of monitoring and remedial measures. These improvements, to February 1988 were summarized in a report on the "Implementation of Recommendations of the 1986 St. Clair River Pollution Investigation Report" released in February 1988 (MOE/DOE 1988).

Many industries in the "Chemical Valley" have upgraded their spill prevention/containment facilities as well as waste treatment and process/cooling water separation.

Specific remedial measures at Dow Chemical have included construction of wastewater containment reservoirs, a riverfront barrier slurry wall and extraction well system. Other improvements were implemented at various process plants including the styrene, solvent and latex plants which enable containment and recycling of stormwater runoff.

As part of these improvements, several process units at Dow Chemical have been re-routed through the Block 90 retention pond. Prior to June 1986, the solvents plant stream was discharged to the Block 90 pond. Effluent from the vinyl chloride plant was re-routed to the Block 90 pond as of November 1986.

A number of recommendations were made regarding contaminated discharge from the Cole drain which receives urban and rural drainage as well as treated and untreated leachate and runoff from landfill sites adjacent to the Scott Road.

Several investigative follow-up studies were initiated by the Ministry of the Environment to document sources to the Cole drain and Scott Road drains. The reader is referred to the co-operative MOE/DOE report (1988) for further details.

(iii) Trends in Contaminant Levels: May 1986 to March 1987

Detailed findings from the long-term effluent monitoring program with brief summary statistics of measured concentrations and loadings are presented in Appendix 1.

Table 4.1.2 and Figures 4.1.1 to 4.1.7 summarize these findings for selected parameters. Laboratory method detection limits are indicated as "MDL" on these figures.

Measured concentrations are extremely variable and appear to be relatively independent of precipitation. The highest and most variable concentrations were typically observed at the Cole drain and the Dow 42-inch sewer. This variability is reflected by the standard deviations for many parameters which exceed the mean by up to a factor of 8.

Due to such an extreme level of variability, it is difficult to discern trends for many outfalls/parameters. In an attempt to better identify trends, particularly given that some process changes have been implemented at known intervals, a Kruskal-Wallis non-parametric Analysis of Variance (ANOVA) was conducted on the data. For purposes of the analysis, it was assumed that the observations were independent.

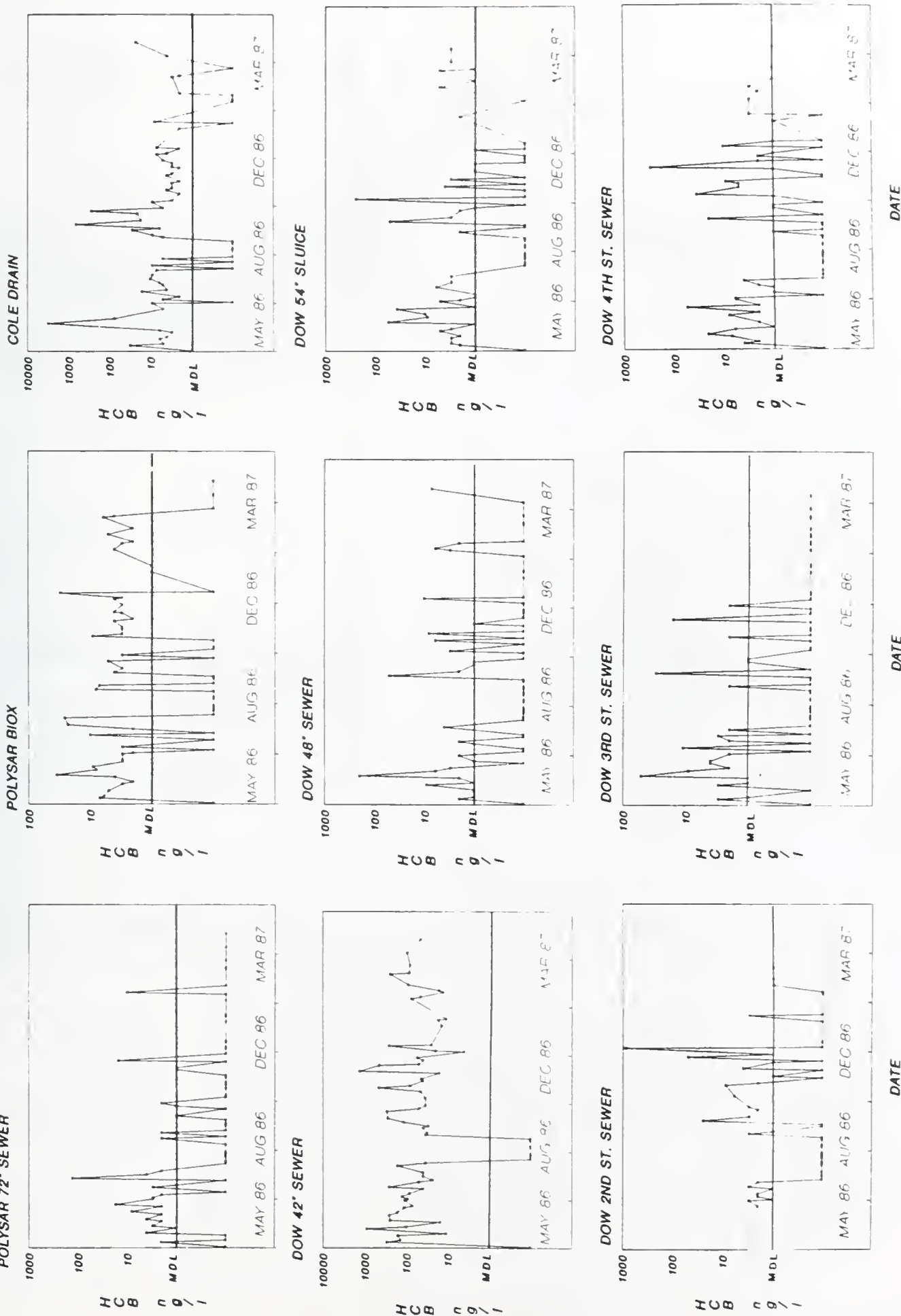
TABLE 4.1.2: LONG-TERM EFFLUENT MONITORING RESULTS - MAY 1986 - MARCH 1987

	Hexachlorobenzene HCB (ng/L)			Hexachlorobutadiene HCBd (ng/L)			Hexachloroethene HCE (ng/L)			Octachlorostyrene OCS (ng/L)			2,4,5-Trichloro- toluene 2,4,5-TCT (ng/L)			Pentachlorobenzene QCB (ng/L)			Carbon Tetrachloride (CCl <sub>4</sub> ) (µg/L)			Tetrachloroethylene PERC (µg/L)		
	MAX	$\bar{X}$	SD	MAX	$\bar{X}$	SD	MAX	$\bar{X}$	SD	MAX	$\bar{X}$	SD	MAX	$\bar{X}$	SD	MAX	$\bar{X}$	SD	MAX	$\bar{X}$	SD	MAX	$\bar{X}$	SD
Outfall																								
Dow 42"	1320	118	201	9500	469	1197	40000	1296	5215	350	52	68	3200	863	934	120	12	19	1326	51	183	539	34	73
Dow 48"	200	5	24	1200	32	147	70	6	12	93	2	12	225	8	30	47	1	6	12	1	2	68	2	11
Dow Sluice	243	7	30	710	39	116	3510	77	424	53	2	7	35	6	8	33	1	5	87	13	16	19	3	3
Dow 2nd St.	870	16	115	3100	75	415	1080	27	144	230	5	31	1700	35	227	70	2	9	16	3	3	772	16	102
Dow 3rd St.	52	2	8	1500	35	184	70	6	10	79	2	10	37	3	7	56	1	8	20	4	4	7	0	1
Dow 4th St.	290	8	35	260	12	31	2250	88	354	41	1	5	81	4	11	10	0	1	28	2	4	12	2	3
Polyser 72"	130	3	16	360	32	46	7	1	1	170	5	21	2	0	0	45	1	5	6	0	1	10	0	1
Polyser Blox	35	4	7	310	18	51	150	6	20	32	5	7	715	14	87	28	4	7	3	0	0	14	0	2
Cola Drain	3130	66	384	44600	1054	5378	480	51	82	300	9	38	3260	72	394	3240	68	401	2	0	0	5	0	1
OVERALL	3130	26	155	44600	199	1876	40000	176	1811	3910	16	162	3260	114	443	3240	10	136	1326	8	63	772	6	42

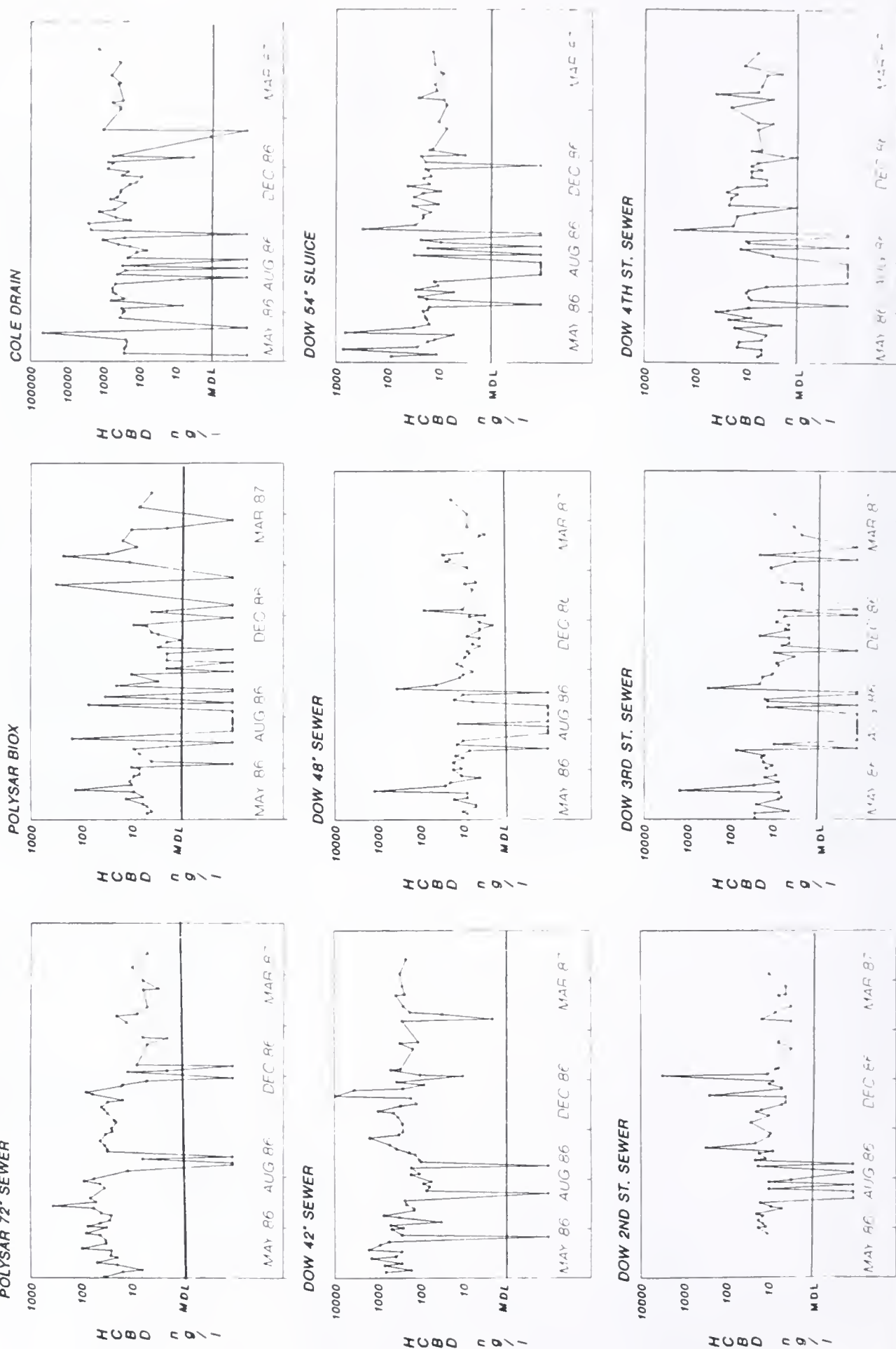
 $\bar{X}$ : Arithmetic mean

SD: Standard deviation

FIGURE 4.1.1  
TWICE-WEEKLY EFFLUENT MONITORING RESULTS  
POLYSAR 72" SEWER

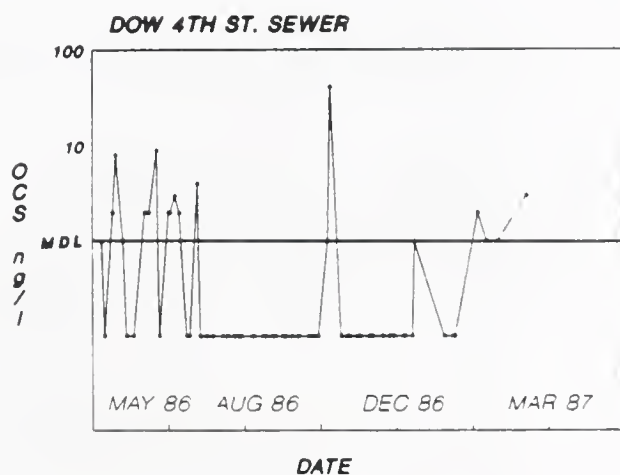
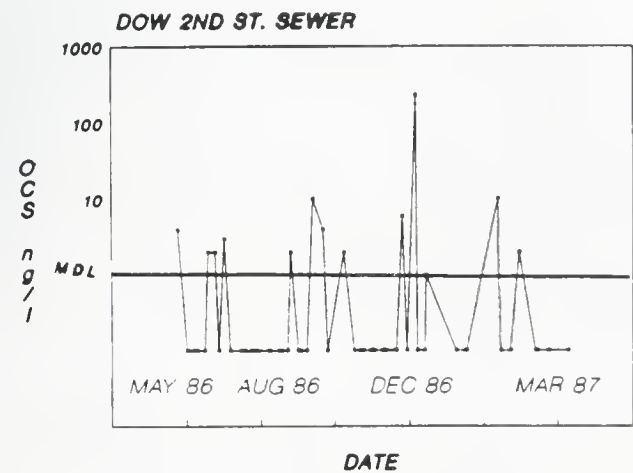
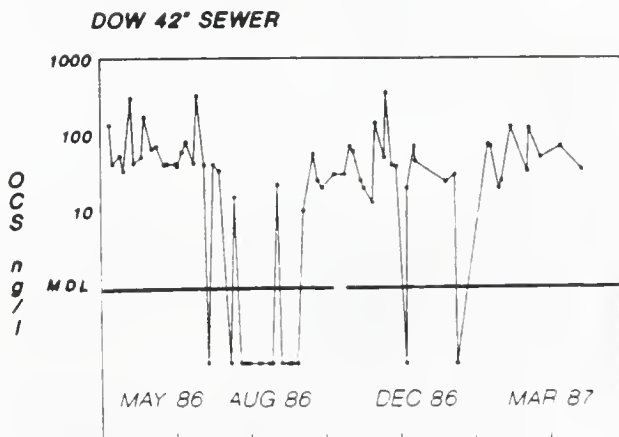
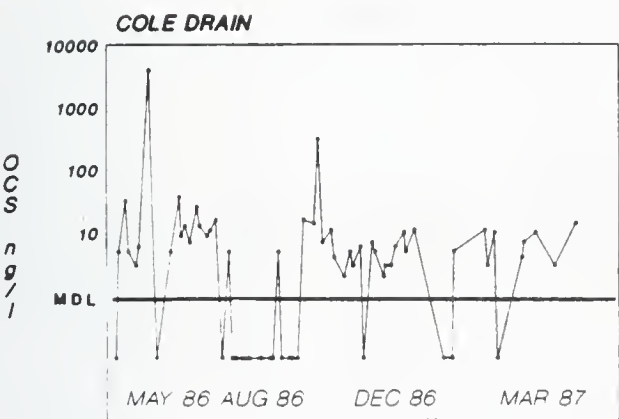
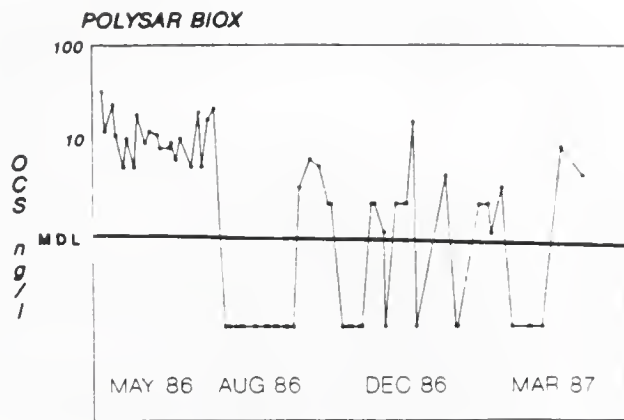
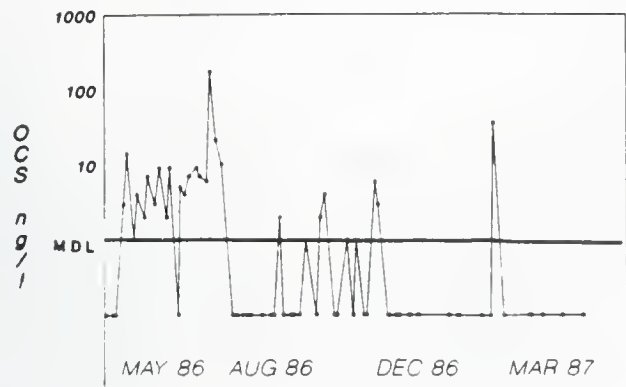


**FIGURE 4.1.2**  
**TWICE-WEEKLY EFFLUENT MONITORING RESULTS**  
**POLYSAR 72" SEWER**



**FIGURE 4.1.3**

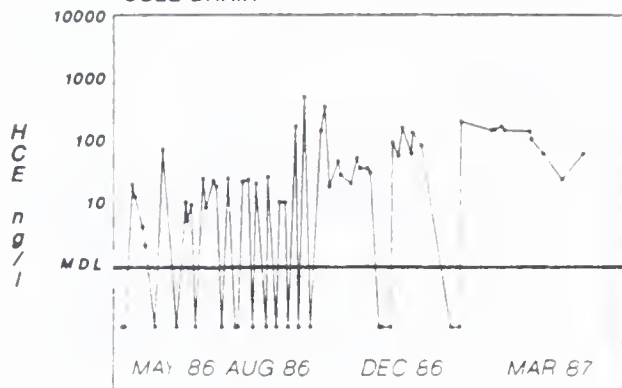
**.TWICE-WEEKLY EFFLUENT MONITORING RESULTS  
POLYSAR 72" SEWER**



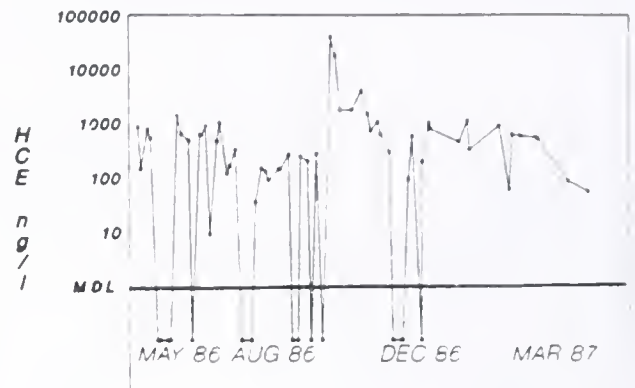


**FIGURE 4.1.4**

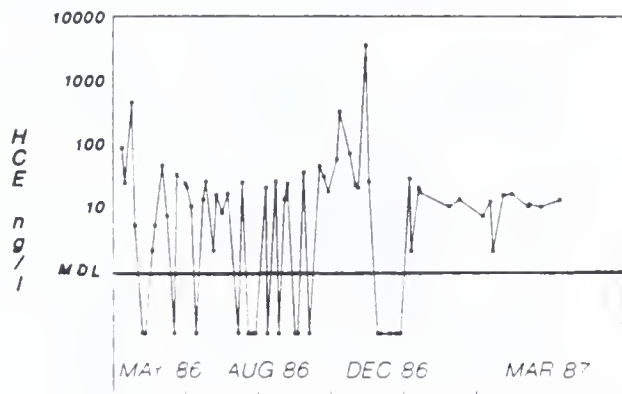
**TWICE-WEEKLY EFFLUENT MONITORING  
COLE DRAIN**



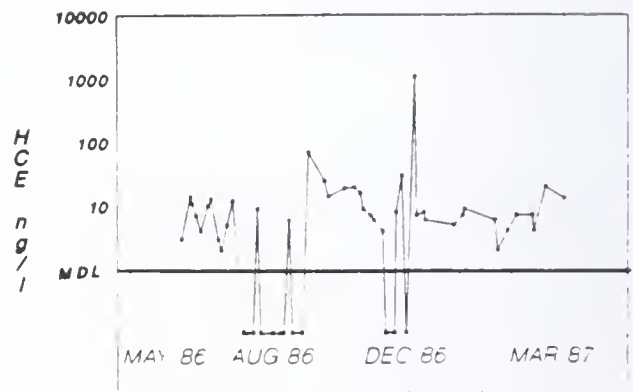
**DOW 42" SEWER**



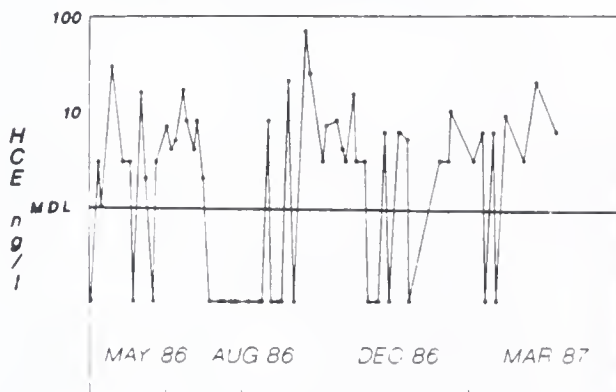
**DOW 54" SLUICE**



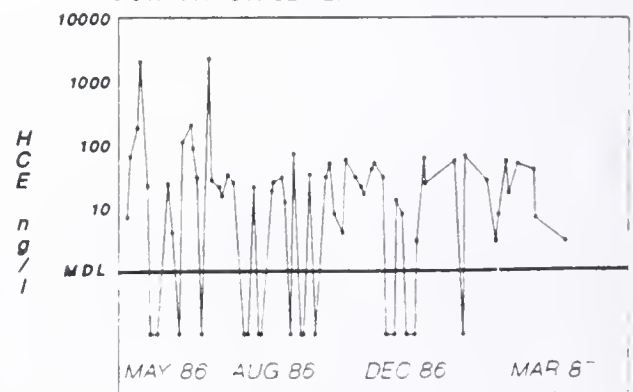
**DOW 2ND ST. SEWER**



**DOW 3RD ST. SEWER**



**DOW 4TH ST. SEWER**

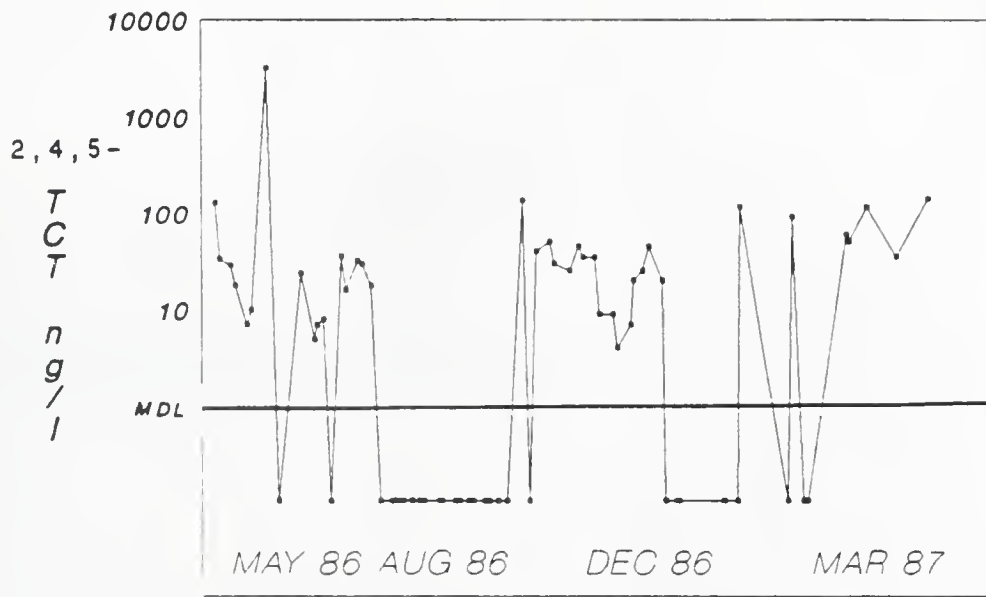


**DATE**

**DATE**



**FIGURE 4.1.5 TWICE-WEEKLY EFFLUENT MONITORING  
COLE DRAIN**



**DOW 42" SEWER**

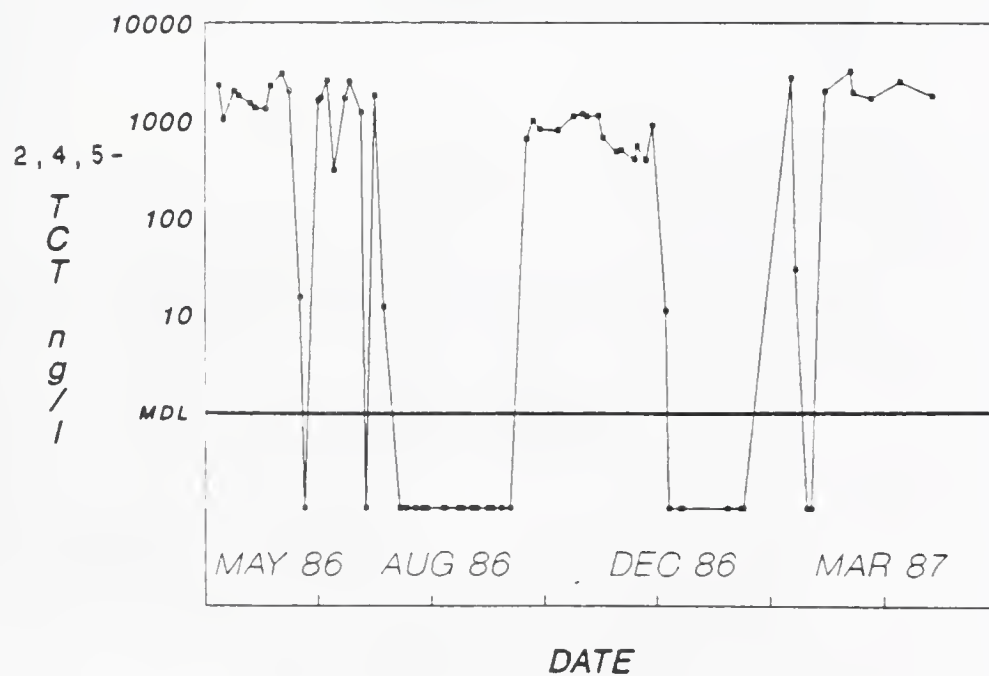
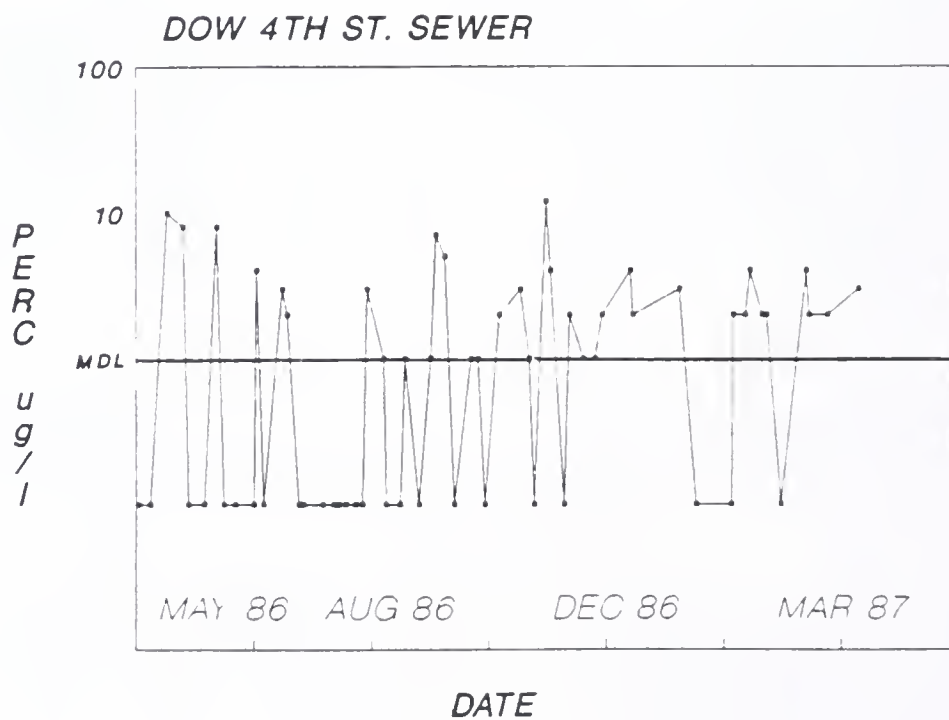
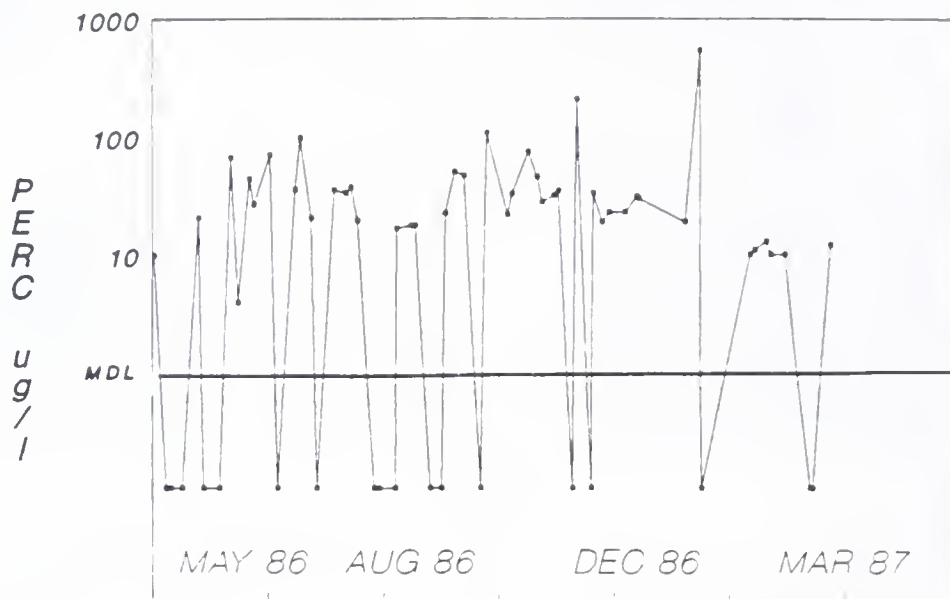
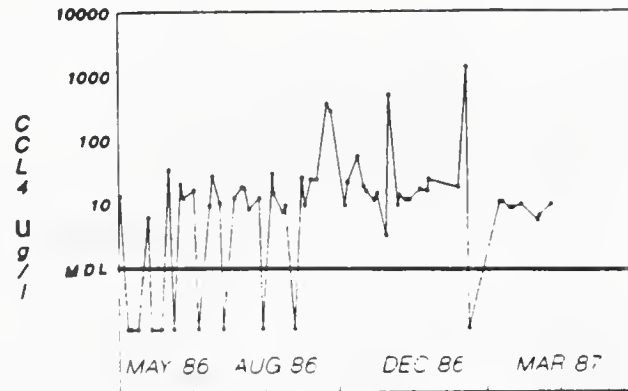


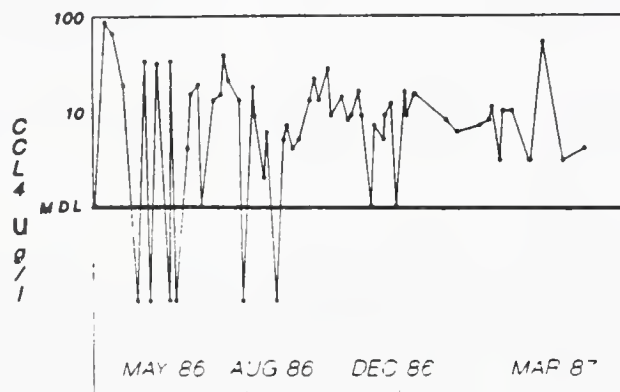
FIGURE 4.1.6 TWICE-WEEKLY EFFLUENT MONITORING  
DOW 42" SEWER



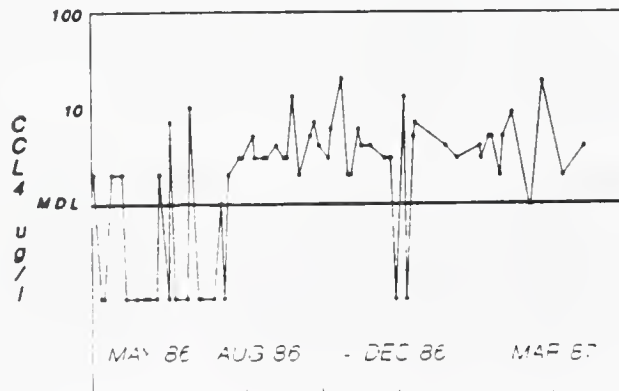
**FIGURE 4.1.7 TWICE-WEEKLY EFFLUENT MONITORING  
DOW 42" SEWER**



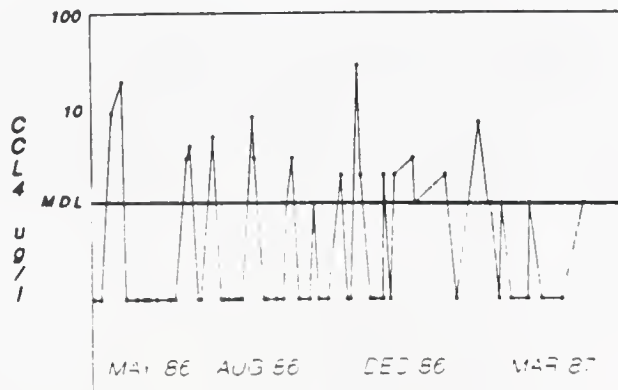
**DOW 54" SLUICE**



**DOW 3RD ST. SEWER**



**DOW 4TH ST. SEWER**



DATE

Prior to statistical analysis, the data were divided into several "seasons" or groups based on anticipated seasonal effects or known alterations to the sewer configuration.

The following dates indicate the periods assigned for each season:

Season 1: May 15 - August 31, 1986

Season 2: September 1 - November 30, 1986

Season 3: December 1, 1986 - February 28, 1987

Season 4: March 1 - March 31, 1987

It is important to note that seasons 3 and 4 represent samples obtained subsequent to the Block 90 pond coming on-line.

A significance level of 95% yielded several significant differences between seasons. A visual analysis of selected Box Plots following analysis of variance identified several increasing or decreasing trends, a number of which are highlighted in Figures 4.1.8 to 4.1.12.

Table 4.1.3 provides a summary of results for which significant differences between seasons ( $p < 0.05$ ) were noted.

Increased concentrations of 1,1-and 1,2-dichloroethane at the 4th St. sewer, and a concurrent rise in levels at the 42-inch sewer (with the exception of a marginal rise in 1,2-dichloroethane) are consistent with the diversion of process water exiting the vinyl chloride plant in November 1986, to the Block 90 pond.

Additional trends were noted at a number of outfalls, largely representing changes in conventional parameter levels. These are identified in Table 4.1.4. Trends observed at the Dow 42-inch sewer and 4th St. sewers may be attributed to changes in sewer configuration referred to previously.

TABLE 4.1.3: LONG-TERM EFFLUENT MONITORING: SUMMARY OF NON-PARAMETRIC ANOVA RESULTS FOR STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN SEASONS (MAY 1986 - MARCH 1987)

STATION	PARAMETER	INCREASE ( $\infty$ )	DECREASE ( $\infty$ )
POLYSAR 72"	Octachlorostyrene		✓ ( $1.8 \times 10^{-6}$ )
POLYSAR 72"	Hexachlorobenzene		✓ ( $2.5 \times 10^{-5}$ )
POLYSAR 72"	Hexachlorobutadiene		✓ ( $6.2 \times 10^{-5}$ )
DOW 42"	1,1-Dichloroethane		✓ ( $2.5 \times 10^{-4}$ )
DOW 42"	1,1,2-Trichloroethane		✓ (0.021)
DOW 42"	1,2-Dichloroethane	✓ (0.04) <sup>1</sup>	
DOW 42"	1,1,2,2-Tetrachloroethane	✓ ( $4.3 \times 10^{-3}$ )	
DOW 48"	Hexachloroethane	✓ ( $1.5 \times 10^{-3}$ )	
DOW 54"	Mercury		✓ ( $9.9 \times 10^{-6}$ )
DOW 3RD ST.	Hexachlorobenzene		✓ ( $2.7 \times 10^{-4}$ )
	Carbon tetrachloride	✓ ( $2.3 \times 10^{-4}$ ) <sup>2</sup>	
DOW 4TH ST.	1,1-Dichloroethane	✓ ( $6.8 \times 10^{-7}$ ) <sup>3</sup>	
	1,2-Dichloroethane	✓ ( $5.5 \times 10^{-5}$ ) <sup>3</sup>	

✓ Indicates significant increasing or decreasing trend between seasons.

1. Marginal significance at  $P < 0.05$  level.
2. Increase noted subsequent to August 31, 1986.
3. Increase noted subsequent to November 30, 1986.

TABLE 4.1.4: PARAMETERS EXHIBITING VISUAL TRENDS (increasing or decreasing) WITH TIME,  
 CONFIRMED BY STATISTICALLY SIGNIFICANT ( $P < 0.05$ ) DIFFERENCES IDENTIFIED  
 IN EFFLUENT QUALITY AT MEASURED SEWERS MAY 1986 – MARCH 1987

OUTFALL	Alkalinity	Conductivity	DIC	Calcium	Chloride	Kjeldahl Nitrogen	Ammonium	Nitrite
POLYSAR 72"								
POLYSAR BIOX	↓					↓	↓	↓
COLE DRAIN		↑		↑			↓	↓
DOW 42"		↓			↓			
DOW 48"						↓		
DOW 54"			↑			↓		
DOW 2ND ST.								
DOW 3RD ST.			↑		↓	↓		
DOW 4TH ST.	↑	↑	↑			↓		

LEGEND: ↑ Significant increase at  $\alpha = 0.05$  level (comparison-wise error rate).  
 ↓ Significant decrease at  $\alpha = 0.05$  level (comparison-wise error rate).  
 DIC – Dissolved Inorganic Carbon

# POLYSAR 72 INCH SEWER

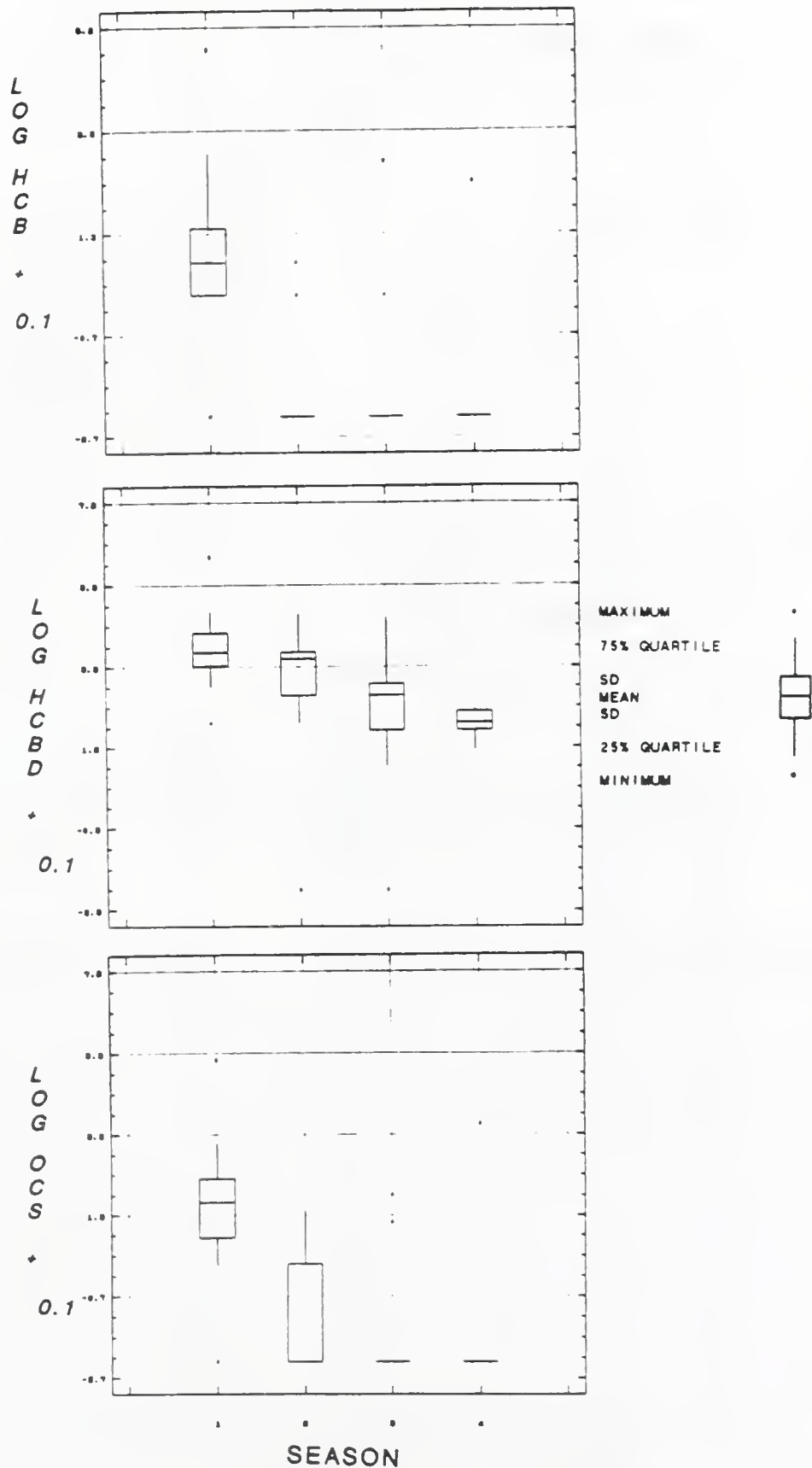


FIGURE 4.1.8 : RESULTS OF NON-PARAMETRIC ANOVA FOR SELECTED PARAMETERS (ng/L)



# DOW 42 INCH SEWER

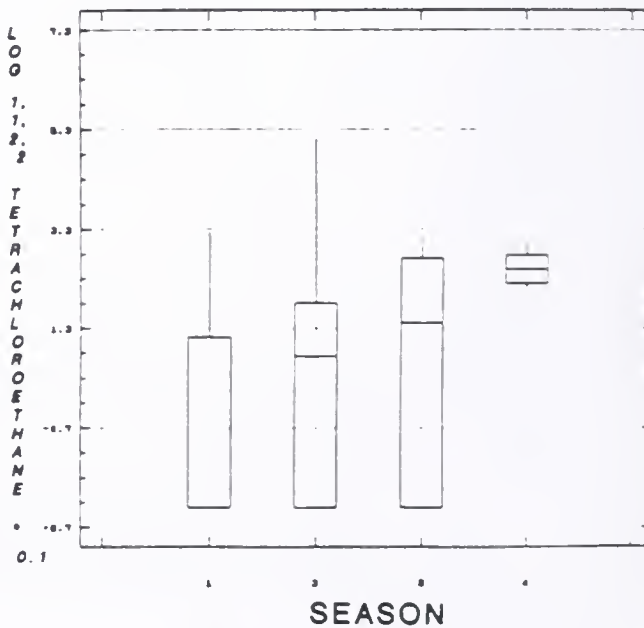
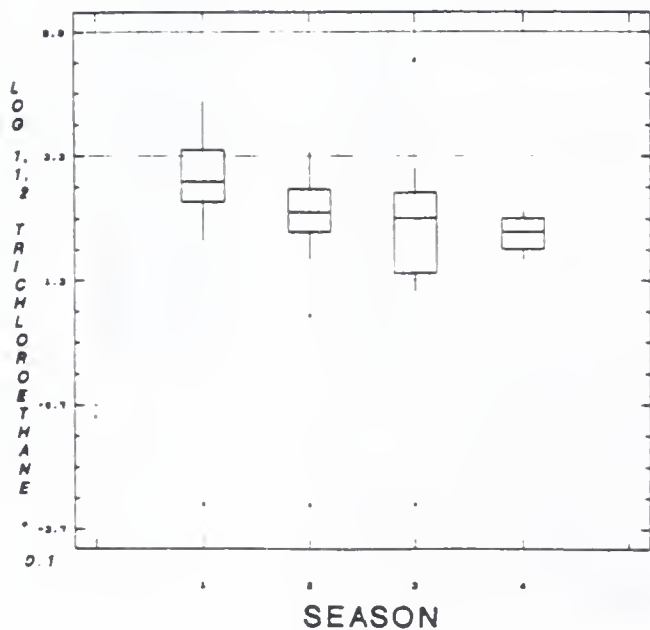
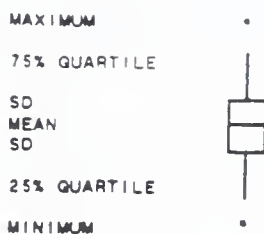
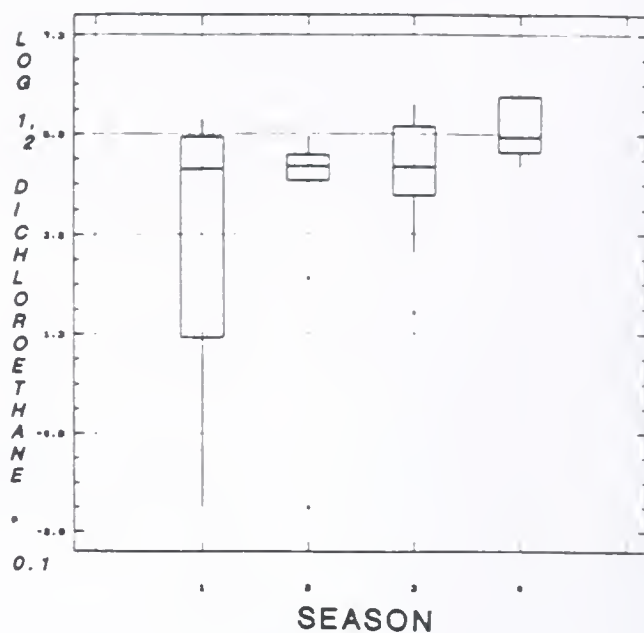
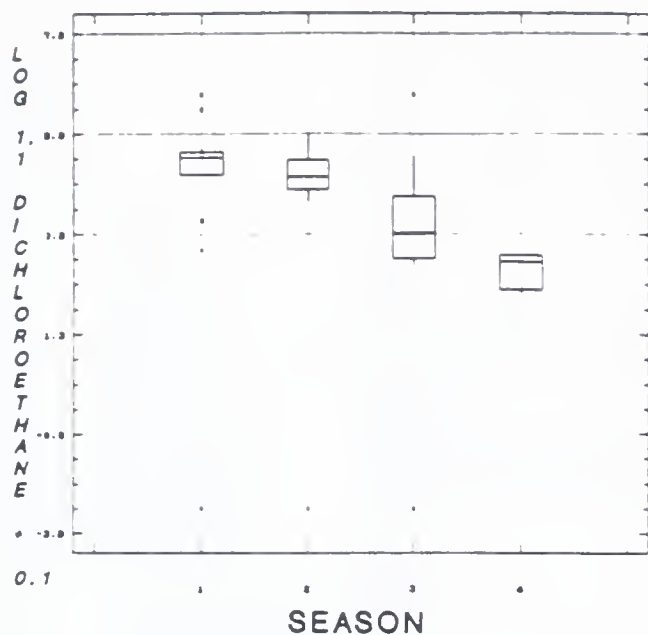
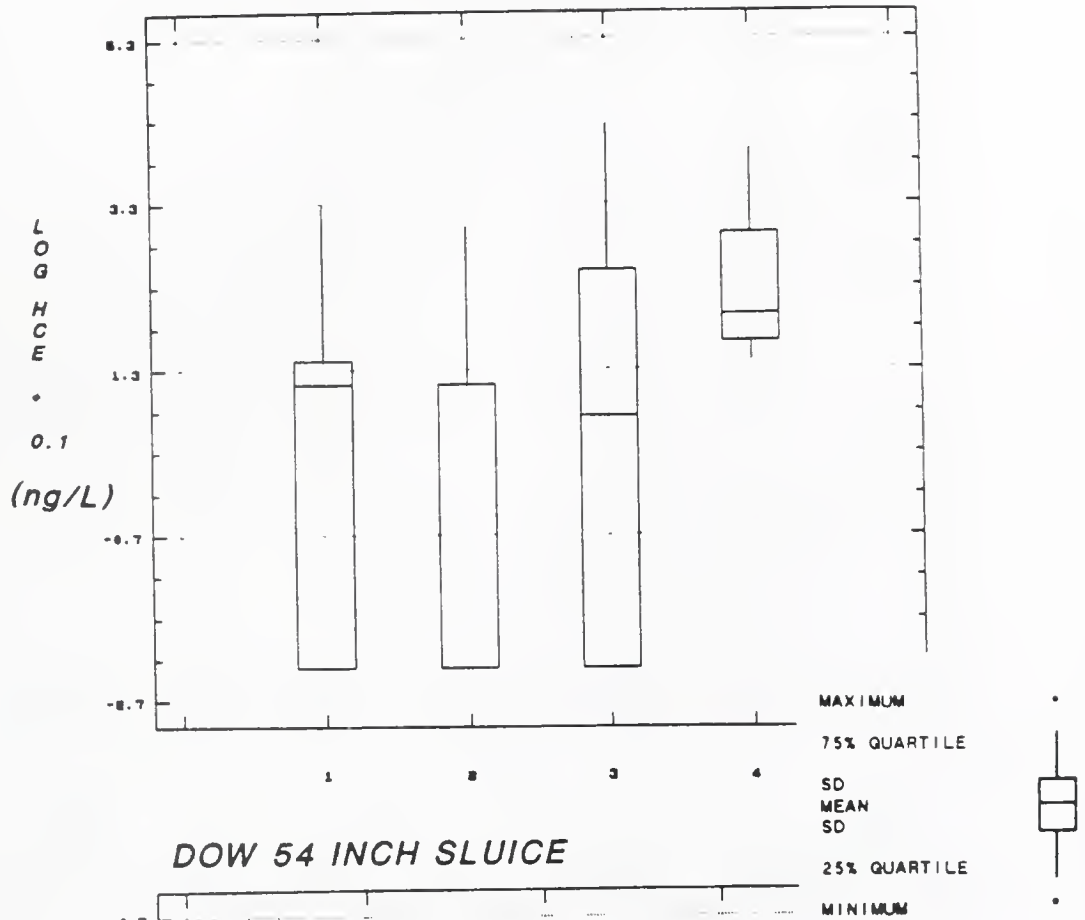


FIGURE 4.1.9 : RESULTS OF NON-PARAMETRIC ANOVA FOR SELECTED PARAMETERS( $\mu\text{g/L}$ )

# DOW 48 INCH SEWER



# DOW 54 INCH SLUICE

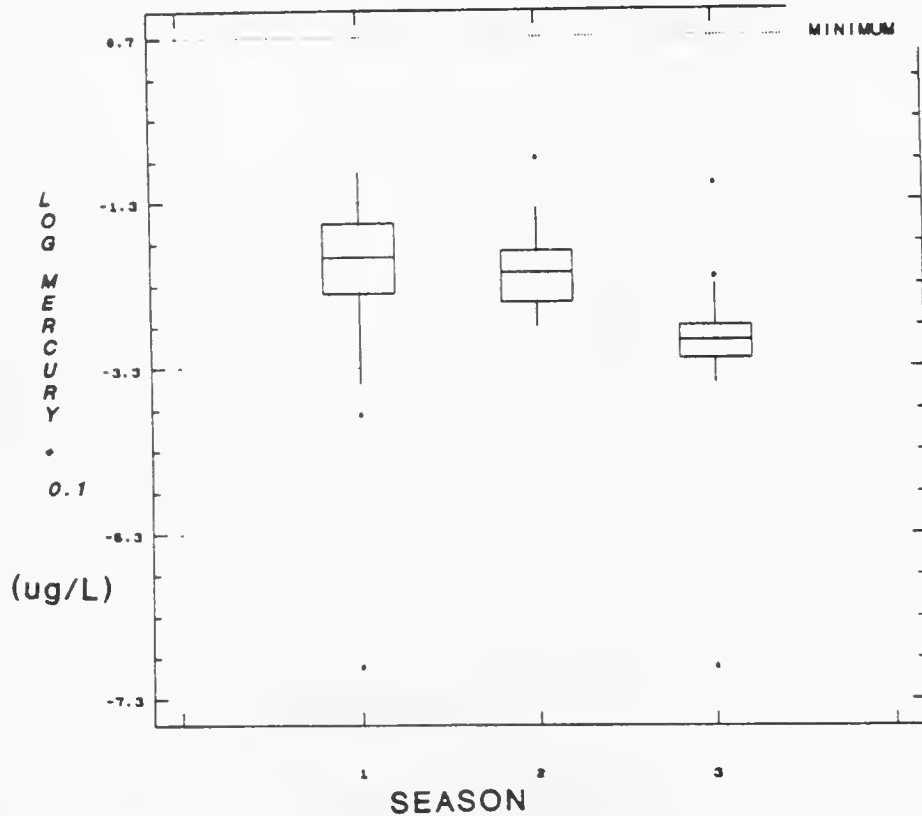


FIGURE 4.1.10 : RESULTS OF NON-PARAMETRIC ANOVA FOR SELECTED PARAMETERS

# DOW 3RD ST. SEWER

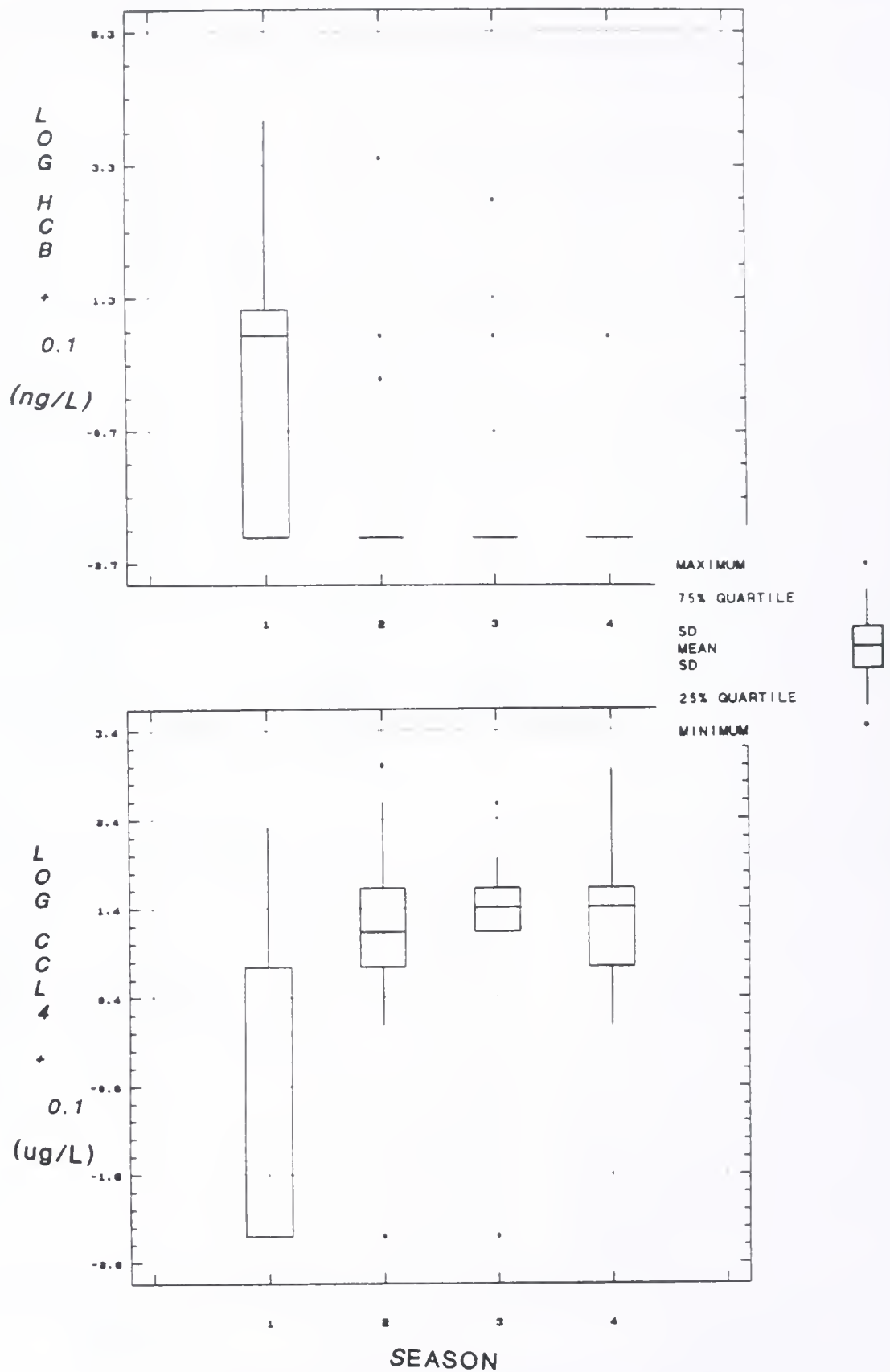


FIGURE 4.1.11 : RESULTS OF NON-PARAMETRIC ANOVA FOR SELECTED PARAMETERS

# DOW 4TH ST. SEWER

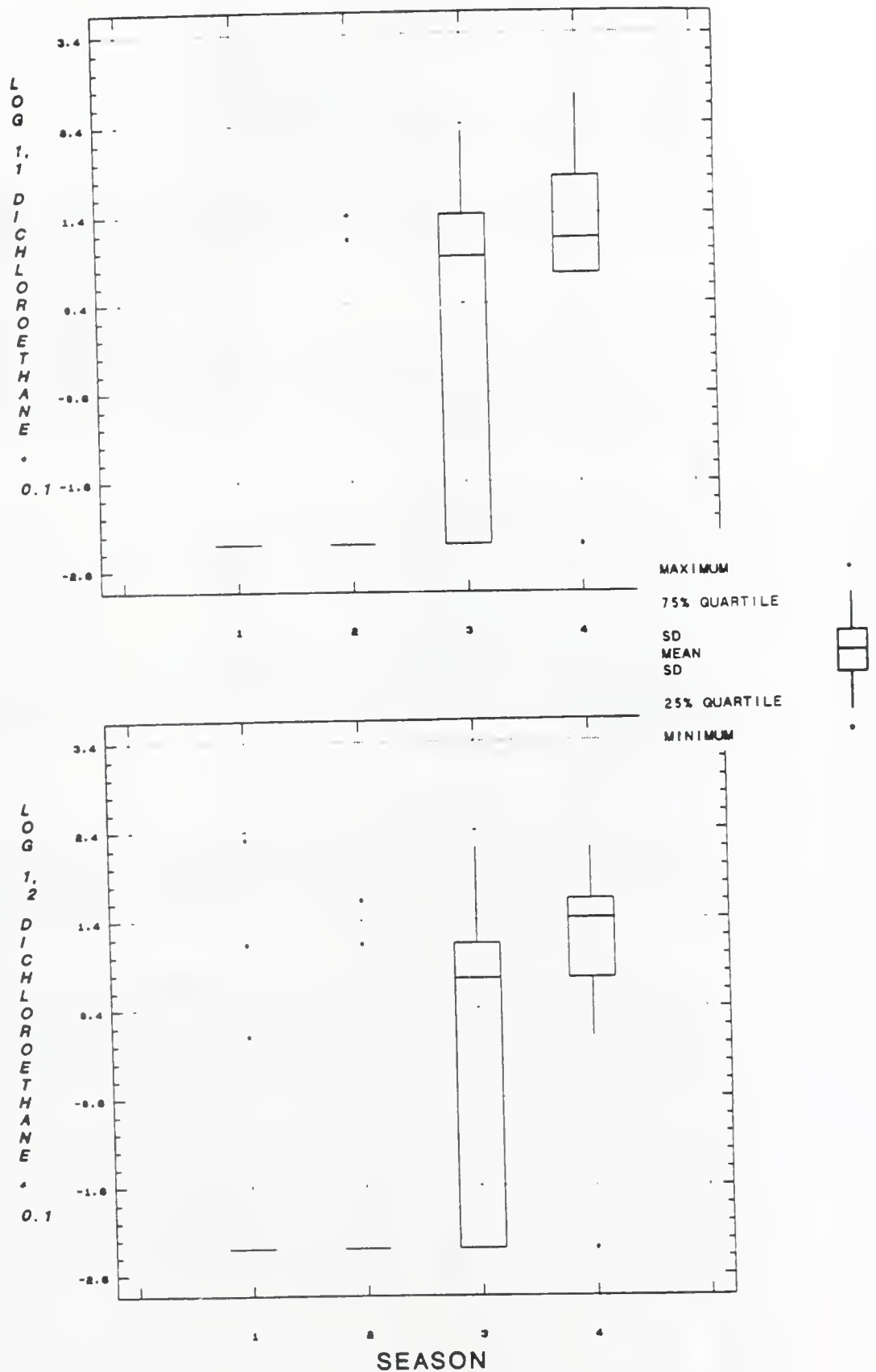


FIGURE 4.1.12 : RESULTS OF NON-PARAMETRIC ANOVA FOR SELECTED PARAMETERS (ug/L)

(iv) Estimation of Loadings

The Ministry reported preliminary findings from the St. Clair River MISA pilot site in November 1987 (MOE 1987). The report highlighted significant reductions in contaminant loadings to the St. Clair River from Dow Chemical during the period November 1985 to September 1986. Tables 4.1.5 and 4.1.6 and Figures 4.1.13 (a and b) and 4.1.14 (a and b) document loadings observed in late 1985 compared with average loadings estimated for the period May 1986 to March 1987.

Additional effluent monitoring to March 1987 and in May 1988 by the Ministry, coupled with ongoing self-monitoring by Dow Chemical provided more current insight into the quality of effluent discharged to the St. Clair River.

Contaminant Loadings have been reduced substantially since late 1985. Figures 4.1.15 to 4.1.21 present long-term monthly effluent monitoring results for selected parameters at several outfalls during the period April 1986 to May 1987. Where available, self-monitoring data from Dow Chemical; data from a short term MOE investigation (May 1988) and November 1985 (DOE/MOE 1986) loadings have been included for comparative purposes.

Loadings were calculated using mean monthly discharge rates for each outfall as supplied to the Industrial Monitoring Information System (IMIS) (MOE 1988a) multiplied by mean monthly concentrations.

This method has been demonstrated by Chapman et al. (1989) to introduce only minor biases in estimating loadings if flow measurements are not coincident with each sample obtained.

Loadings of the various sewers tested relative to the Dow 42-inch outfall confirm the importance of both the 42-inch sewer as well as the Cole drain. It is important to note the magnitude of contaminants such as QCB, HCB, HCBd, OCS, lead and cadmium entering the St. Clair River through the Cole drain (Table 4.1.7).

TABLE 4.1.1.5: LOADINGS OF COMPOUNDS (g/day) ENTERING THE ST. CLAIR RIVER FROM THE COLE DRAIN  
AND DOW CHEMICAL SEWERS: 1985, 1986/87

LOADINGS (g/day) CHLORINATED AROMATICS:	COLE DRAIN		1ST ST. 42"		1ST ST. 48"		1ST ST. 30"		1ST ST. 54"		2ND ST.		3RD ST.		4TH ST.	
	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87
1,2,3,4 - TETRACHLOROBENZENE	1.4	0.62	1.7	0.14	--	0.002	0.06	--	0.002	0	0.3	0	0.3	0.032	--	0.015
1,2,3,5 - TETRACHLOROBENZENE	2.8	0.58	0.7	0.02	--	0.006	0.3	--	0.002	0.007	0.3	0.007	0.3	0.05	--	0
1,2,4,5 - TETRACHLOROBENZENE	1.05	0.85	--	0.05	--	0.007	0.2	--	0	0.008	--	0.008	--	0.005	--	0.07
1,2,4 - TRICHLOROBENZENE	322	1.89	384	2.88	1.1	0.03	43	2.7	0.07	0.63	5.5	0.63	2.3	0.39	12	0.49
1,2,3 - TRICHLOROBENZENE	1.15	13.93	0.5	0.04	--	0	0.01	--	0	0.03	--	0.03	0.7	0.07	--	0.06
1,3,5 - TRICHLOROBENZENE	23.8	1.04	7.2	0.34	--	0.03	2.7	--	0.01	0.002	0.5	0.002	0.4	0.06	--	0.05
2,3,6 - TRICHLOROTOLUENE	NM	0.03	NM	0	NM	0	NM	NM	0	0	NM	0	NM	0.01	NM	0
2,4,5 - TRICHLOROTOLUENE	NM	9.54	NM	48.11	NM	0.37	NM	NM	0.16	1.92	NM	1.92	NM	0.23	NM	1.4
2,6, - a - TRICHLOROTOLUENE	NM	0.05	NM	0.58	NM	0.001	NM	NM	0	0	NM	0	NM	0.05	NM	0
HEXACHLOROBENZENE	2.52	8.88	91	6.88	1	0.28	28	0.6	0.22	0.3	1	1	1.1	0.14	2.9	3.3
HEXACHLOROBUTADIENE	210	140.3	188.5	28.22	0.9	1.81	19	1.8	1.19	4.08	1.2	4.08	1.9	2.04	2.6	4.61
HEXACHLOROETHANE	57.4	6.81	130	77.42	0.5	0.3	28	21.6	2.43	1.1	1.48	1.48	1.6	0.42	3.5	36.96
OCTACHLOROSTYRENE	0.59	9.16	2.7	2.91	0.1	0.13	1.6	0.1	0.05	--	--	0.27	0.1	0.15	0.2	0.54
PENTACHLOROBENZENE	3.22	9.1*	3	0.66	--	0.06	1	--	0.03	0.08	--	0.08	0.7	0.1	0.1	0.12
TOTALS	625.93	202.78	809.30	168.25	3.60	3.03	123.87	26.80	4.16	9.20	9.51	9.51	9.40	3.75	21.30	47.62

DOW COMPLEX TOTALS: 1985 - 1003.5 g/day  
1986/87 - 236.3 g/day

\* Includes single elevated value of 3910 ng/L (567 g/day) following 66.2 mm rainfall on 2 previous days.  
- 1985 data from DOE/MOE (1986)

NM = not measured  
-- = not detected

TABLE 4.1.6: LOADINGS OF COMPOUNDS (kg/day) ENTERING THE ST. CLAIR RIVER FROM THE COLE DRAIN AND DOW CHEMICAL SEWERS:  
1985, 1986/87

LOADINGS (kg/day) VOLATILES:	COLE DRAIN		1ST ST. 42"		1ST ST. 48"		1ST ST. 30"		1ST ST. 54"		2ND ST.		3RD ST.		4TH ST.	
	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87	1985	1986/87
1,1 - DICHLOROETHANE	0.504	0.0576	0.36	3.95074	--	0.16542	4.6	0.00373	0.13	0.00373	--	0.01271	--	0.00108	--	0.00037
1,1 - DICHLOROETHYLENE	--	--	NM	0.32926	NM	0.00316	NM	0.00294	NM	0.00294	NM	0.0018	NM	0.02235	NM	0.01665
1,1,1 - TRICHLOROETHANE	--	0.1311	--	3.94104	--	0.26437	7.1	0.05821	0.57	0.05821	--	0.0544	--	0.07426	--	0.74075
1,1,2 - TRICHLOROETHANE	0.784	0.00199	1.7	0.81921	--	0.02393	1.8	0.00475	0.063	0.00475	--	0.00302	--	0.00606	--	0.03208
1,1,2,2 - TETRACHLOROETHANE	0.308	--	0.91	0.39782	--	0.00923	0.3	--	--	--	--	--	--	--	--	--
1,2 - DICHLOROETHANE	8.96	0.03178	9.1	5.27826	0.12	0.30455	9.2	0.07252	0.51	0.07252	--	0.14522	--	0.02576	--	0.5333
1,3 - DICHLOROETHANE	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1,4 - DICHLOROETHANE	0.7	--	0.0338	--	--	--	0.0047	--	--	--	--	--	--	--	--	--
ACROLEIN	--	NM	--	NM	--	NM	--	NM	--	NM	--	NM	--	NM	3.9	NM
ACRYLONITRILE	--	NM	--	NM	--	NM	--	NM	--	NM	--	NM	--	NM	2.9	NM
BENZENE	--	0.00397	0.052	0.12588	--	0.02133	0.044	0.01911	--	0.01911	--	0.02511	58	0.26936	3.9	0.16656
BROMOFORM	--	0.25226	--	0.01038	--	0.00133	--	0.03188	--	0.03188	--	0.00296	--	--	--	0.03064
CARBON TETRACHLORIDE	--	0.00795	3.8	2.57346	--	0.04125	10	0.35758	0.81	0.35758	0.099	0.18564	11	0.25307	--	0.6755
CHLOROBENZENE	--	--	--	0.06878	--	--	--	--	--	--	--	0.00088	--	0.07075	--	0.02045
CHLOROFORM	3.78	1.07062	1.1	0.09818	--	0.00734	0.42	0.02856	--	0.02856	--	0.01921	--	0.03115	--	0.15312
ETHYLBENZENE	--	--	--	--	--	--	--	--	--	--	--	--	60	2.59	9.6	--
STYRENE *	--	--	--	0.2	--	--	--	0.03	--	0.03	--	0.003	120	2.36	--	0.1
TETRACHLOROETHYLENE	0.462	0.04767	6.3	1.70057	--	0.08695	7.1	0.4051	0.71	0.4051	0.073	0.1526	--	0.02503	--	0.68354
TOTALS:	15.498	1.60494	23.3558	19.49358	0.12	0.92886	40.5687	1.01438	2.793	1.01438	0.172	0.60655	249	5.72887	20.3	3.63696

DOW COMPLEX TOTALS: 1985 - 336.31 kg/day  
1986/87 - 33.01 kg/day

\* 1986/87 STYRENE DATA FROM DOW SELF-MONITORING

NM = not measured  
-- = not detected



Loadings calculated from Dow self-monitoring data during the early part of this study were extrapolated from a single monthly grab sample and flow measurement and may not be representative of average monthly operating conditions. Further, loadings may be underestimated in some instances where numerical concentrations could not be determined due to high method detection limits (limit of quantification - LOQ). Values below the LOQ were censored and consequently, loadings were assigned a value of "0". The LOQ, while dependent on the class of compound also appeared to be subject to factors such as dilution of the sample, and was typically 1 to 3 orders of magnitude higher than MOE method detection levels (MDL) below which concentrations were assigned a value of "0".

Dow has more recently (1988) increased outfall sampling frequency to 3 times/week and reduced the LOQ to the low ppt (ng/L) range.

In an effort to better understand the implications of assigning zero values for samples below method detection limits, a brief comparison of alternatives was undertaken. For many data sets, results below detection limits were assigned values of zero, one-half the detection limit, or the detection limit.

The example matrix which follows provides an indication of the significance of different assigned values on loading calculations:

Parameter ( % <MDL)	n	ASSIGNED VALUE FOR <MDL RESULTS					
		0		0.5		1.0	
		Load	$[\bar{x}]$	Load	$[\bar{x}]$	Load	$[\bar{x}]$
HCB (20.6)	68	9.54	[65.76]	9.54	[65.86]	9.57	[65.97] +0.3%
HCBD (10.4)	67	152.86	[1054.22]	152.87	[1054.27]	152.89	[1054.32] +0.01%
OCS (31.3)	67	9.99	[68.87]	10.01	[69.03]	10.03	[69.18] +0.41%

Sewer: Cole drain	Load: g/day
Discharge value: 145000m <sup>3</sup> /day	n: no. of samples
MDL: 1 ng/L	+: increase in load from assigning MDL instead of zero
	[ $\bar{X}$ ]: mean conc'n in ng/L

The number of results below MDL vary from 10 to 31% in this example. The significance of selecting zero instead of the MDL (in this case, 1 ng/L) would tend to underestimate loadings with greater significance attributed to data sets with a marginally higher proportion of <MDL results and/or a lower mean concentration. Neither of these factors appear to seriously underestimate loadings in this example.

Several methods are currently available which predict the mean of a data set given its distribution. Of these methods, the Maximum - Likelihood - Estimator (MLE) method by El-Shaarawi (1988) has been successfully employed using Great Lakes data sets.

The use of a method such as this, avoids the need for selecting an assigned value at or below the method detection limit.

Dow complex loadings were reduced 76 and 90% for total chlorinated aromatic compounds and total volatiles respectively (Tables 4.1.5, 4.1.6) from November 1985 to the 1986-87 sampling period.

Improvements in effluent quality during the long-term monitoring phase of the pilot site study were less obvious. Table 4.1.3 indicated decreasing contaminant levels for OCS, HCB and HCBd at the Polysar 72-inch sewer (Figure 4.1.8). The only significant reductions noted at Dow sewers from May 1986 to March 1987 were for 1,1 - dichloroethane (1,1-DCE) and 1,1,2 - trichloroethane (1,1,2-TCE) at the 42-inch sewer (Figure 4.1.9). This occurred as a result of diversion of process water from the vinyl chloride plant to the Block 90 pond. Mercury at the 54-inch sluice (Figure 4.1.10) and HCB at the 3rd St. sewer (Figure 4.1.11) were also reduced over the sampling period.

TABLE 4.1.7: AVERAGE POINT SOURCE LOADINGS AS A PERCENTAGE OF LOADINGS FROM THE DOW 42-INCH SEWER

Parameter	Dow 42" Load (kg/day)	Dow 48" (%)	Dow 54" (%)	Dow 2nd (%)	Dow 3rd (%)	Dow 4th (%)	Cole Drain (%)	Polysar BIOX (%)	Polysar 72" (%)
HCB	0.007	4.0	3.1	14.1	2.0	47.1	127*	0.5	1.2
HCBd	0.028	6.4	4.3	14.6	7.3	16.4	500*	0.6	2.9
HCE	0.077	0.4	3.1	1.9	0.5	48.1	88.3	0.07	0.03
OCS	0.003	4.3	1.7	9.1	5.0	18.0	307*	1.5	4.3
2,4,5-TCT	0.048	0.8	0.3	4.0	0.5	2.9	19.8	0.2	0.003
QCB	0.0007	8.9	4.3	11.9	14.0	17.1	x13*	5.6	3.0
CCL <sub>4</sub>	2.57	1.6	13.9	7.2	9.8	26.3	0.3	0.02	0.08
PERC	1.70	5.1	3.9	53.4	1.47	40.2	2.8	0.16	0.2
1,1-DCE	3.95	4.1	0.1	0.3	0.03	12.1	1.4	0.008	0.08
1,2-DCE	5.28	5.8	1.4	2.7	0.5	10.1	0.6	0.09	0.7
1,1,1-TCE	3.94	6.7	1.5	1.4	1.9	18.8	3.3	0.25	0.07
1,1,2-TCE	0.82	2.9	0.6	0.4	0.7	3.9	0.23	1.1	1.0
LEAD	0.015	153	313	240	293	x23	x25.7*	420	126
CADMIUM	0.0007	42.9	57.1	571	114	214	x66.4*	429	42.9
MERCURY	0.0007	28.6	500	557	386	914*	314	42.9	14.3
X(excluding metals)	100	4.3	3.2	10.1	3.6	21.8	195.9	0.84	1.1
Rank	2	5	7	4	6	3	1	9	8

LEGEND:  
 x - multiple factor  
 \* - highest mean loading  
 (if other than 42")

FIGURE 4.1.13a : TOTAL CHLORINATED AROMATIC LOADINGS ENTERING THE ST. CLAIR RIVER FROM THE COLE DRAIN AND DOW CHEMICAL SEWERS (g/day)

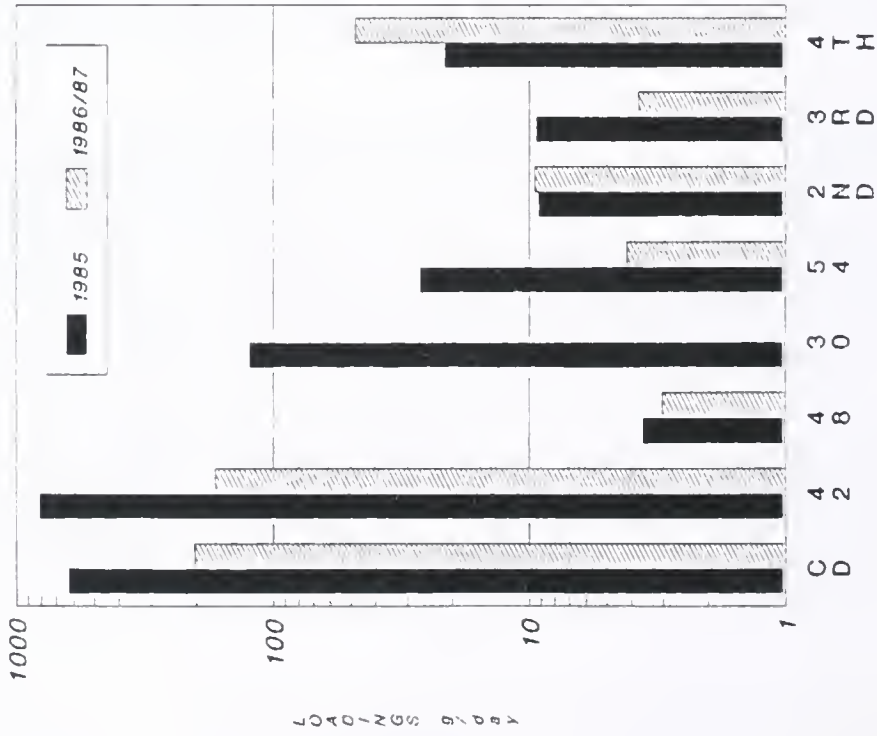
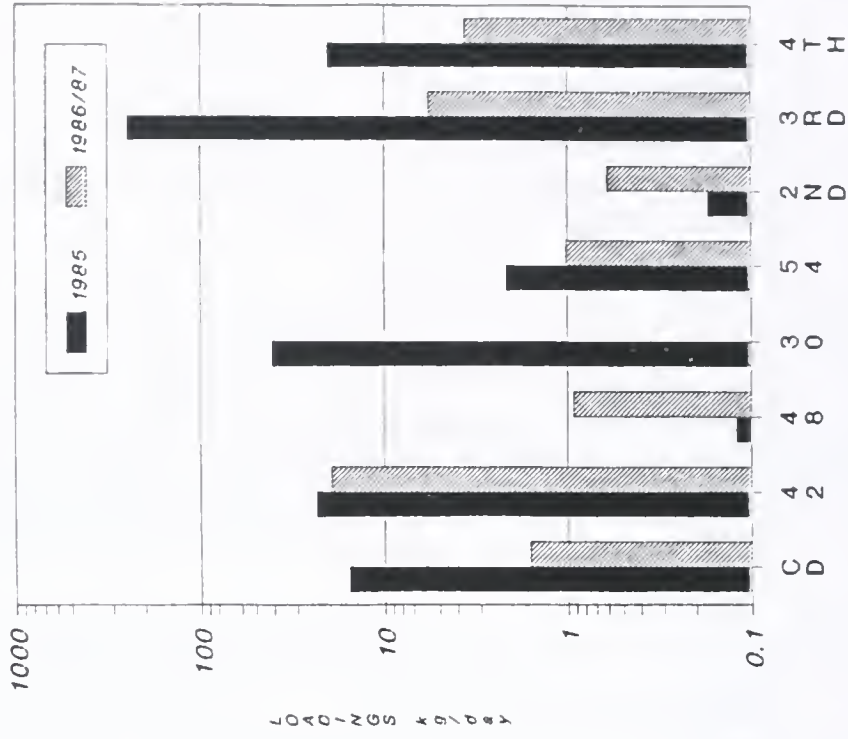


FIGURE 4.1.13b : TOTAL VOLATILE ORGANIC LOADINGS ENTERING THE ST. CLAIR RIVER FROM THE COLE DRAIN AND DOW CHEMICAL SEWERS (g/day)



CD - Cole Drain  
 42 - Dow 42" sewer  
 48 - Dow 48" sewer  
 30 - Dow acid lile drain  
 54 - Dow 54" sewer  
 2nd - Dow 2nd st. sewer  
 3rd - Dow 3rd st. sewer  
 4th - Dow 4th st. sewer

FIGURE 4.1.14a: TOTAL CHLORINATED AROMATIC LOADINGS TO THE ST. CLAIR RIVER FROM DOW CHEMICAL 1985 TO 1987 (g/day)

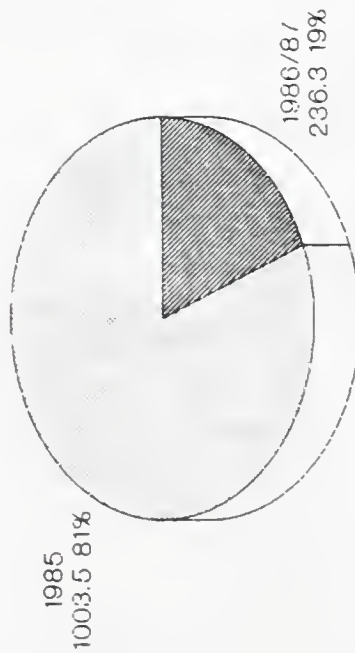


FIGURE 4.1.14b: TOTAL VOLATILE ORGANIC LOADINGS TO THE ST. CLAIR RIVER FROM DOW CHEMICAL 1985 TO 1987 (kg/day)

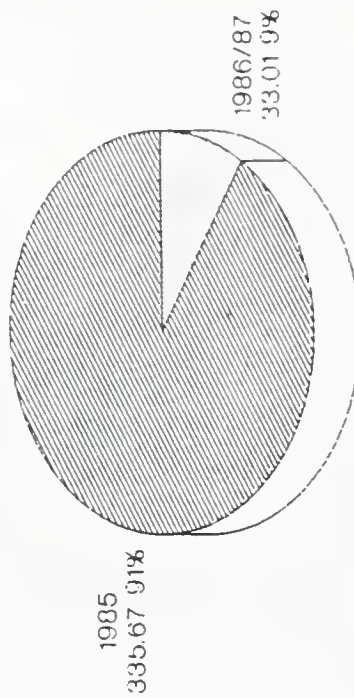


FIGURE 4.1.15: WEEKLY EFFLUENT LOADINGS  
EXPRESSED ON A MONTHLY BASIS

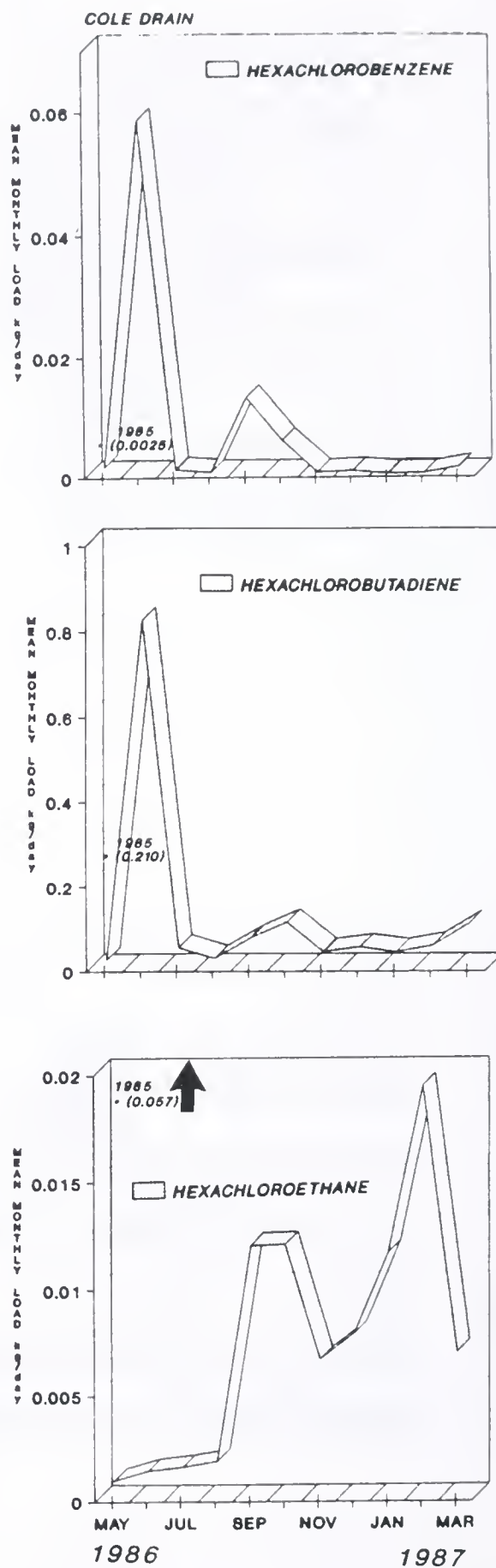
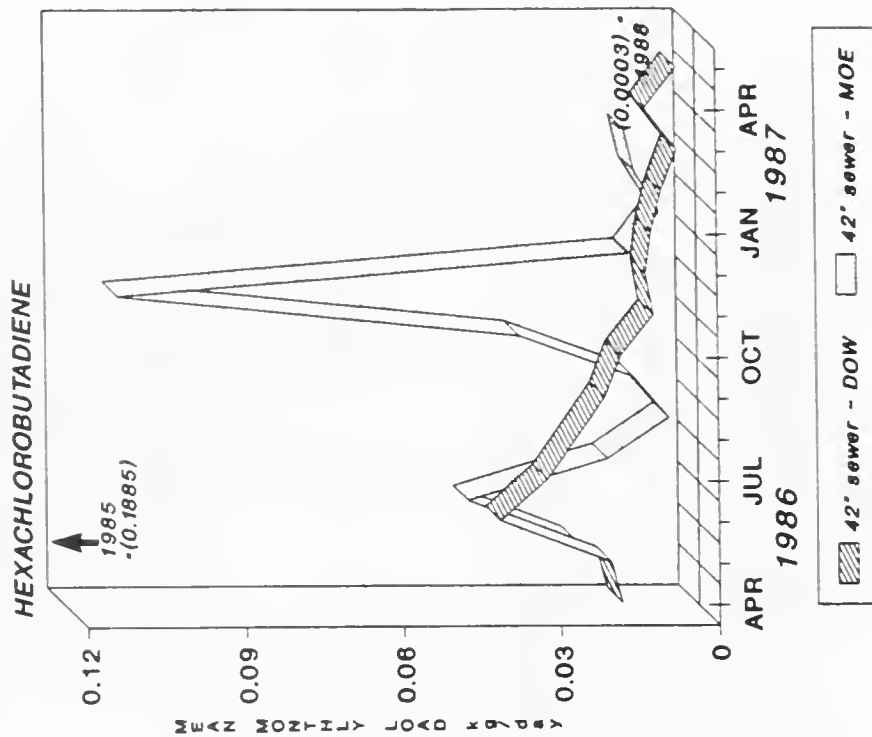
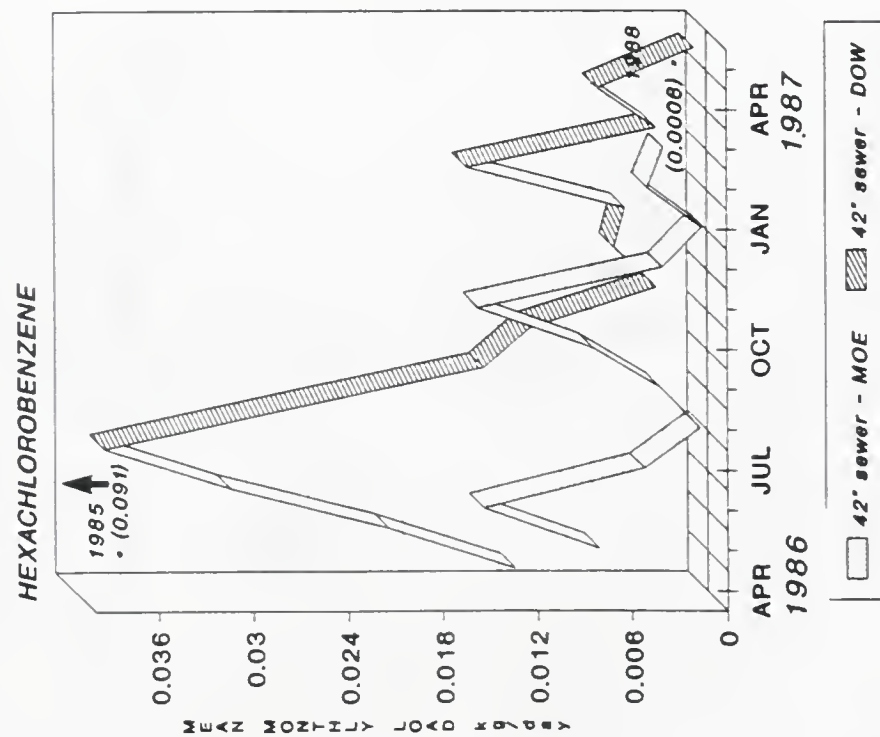




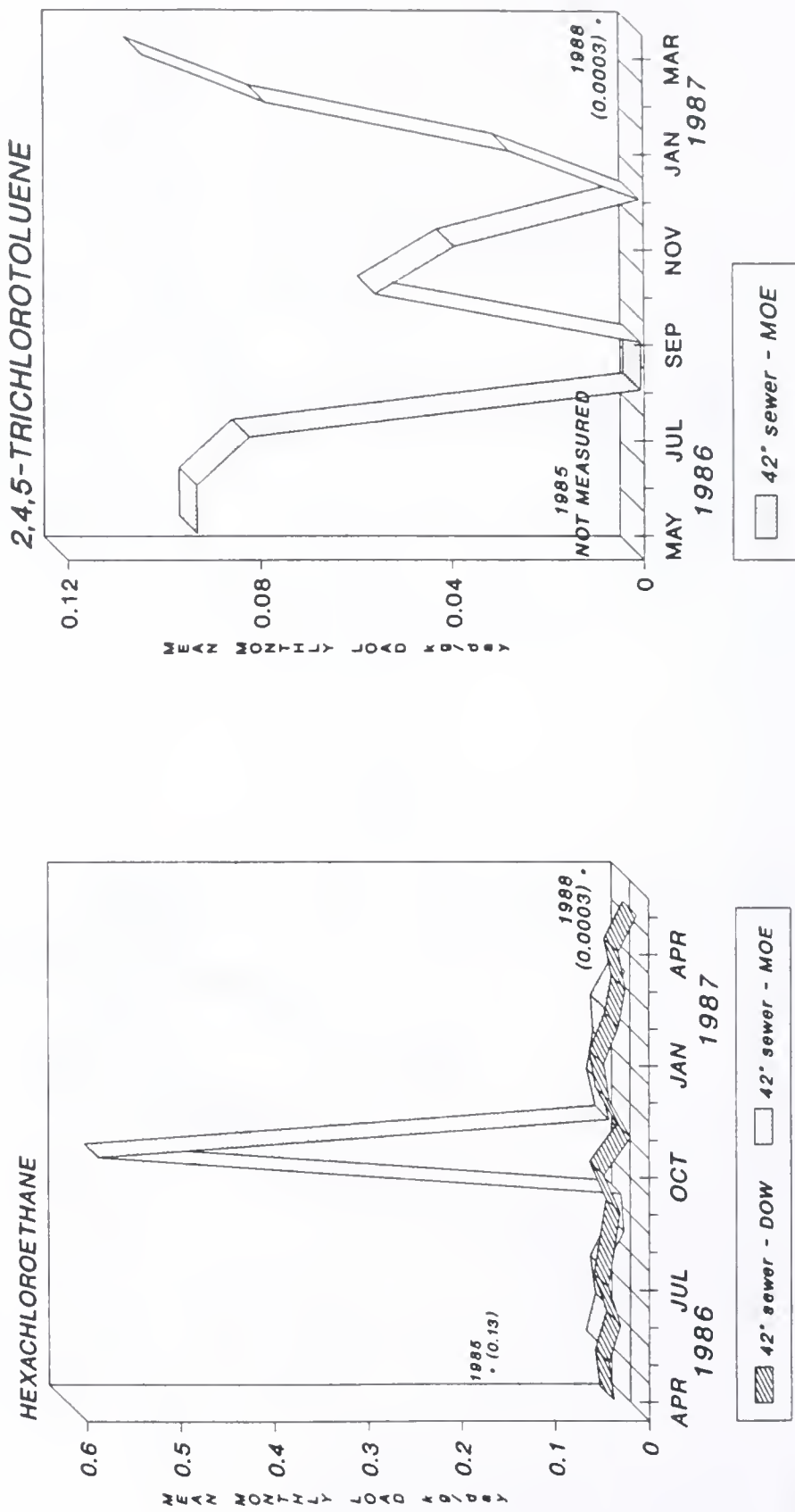
FIGURE 4.1.16: WEEKLY EFFLUENT LOADINGS  
EXPRESSED ON A MONTHLY BASIS



DOW: self-monitoring data  
MOE: long-term effluent monitoring

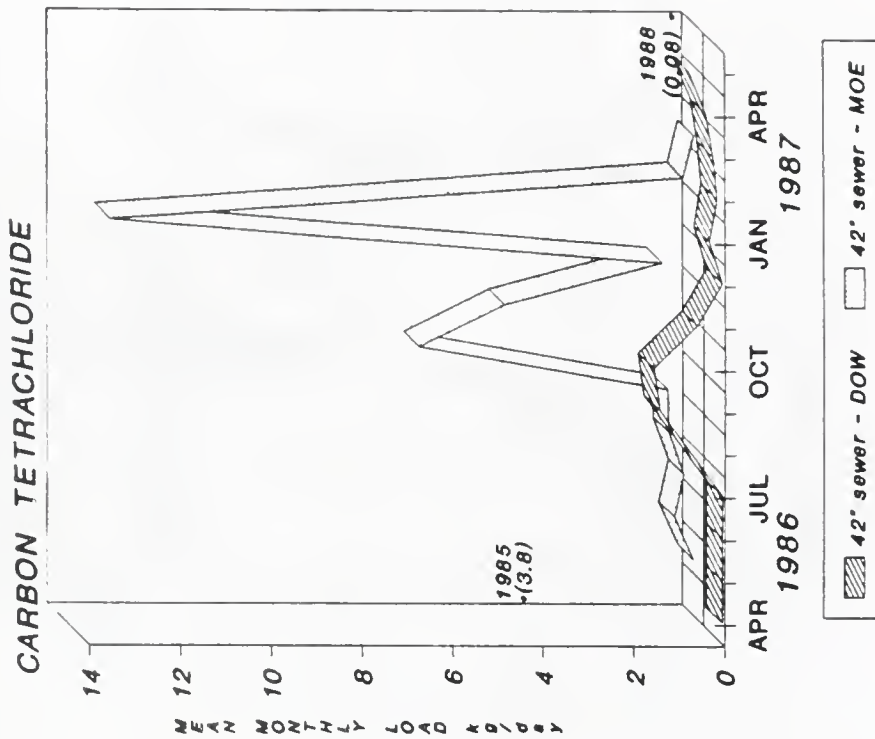
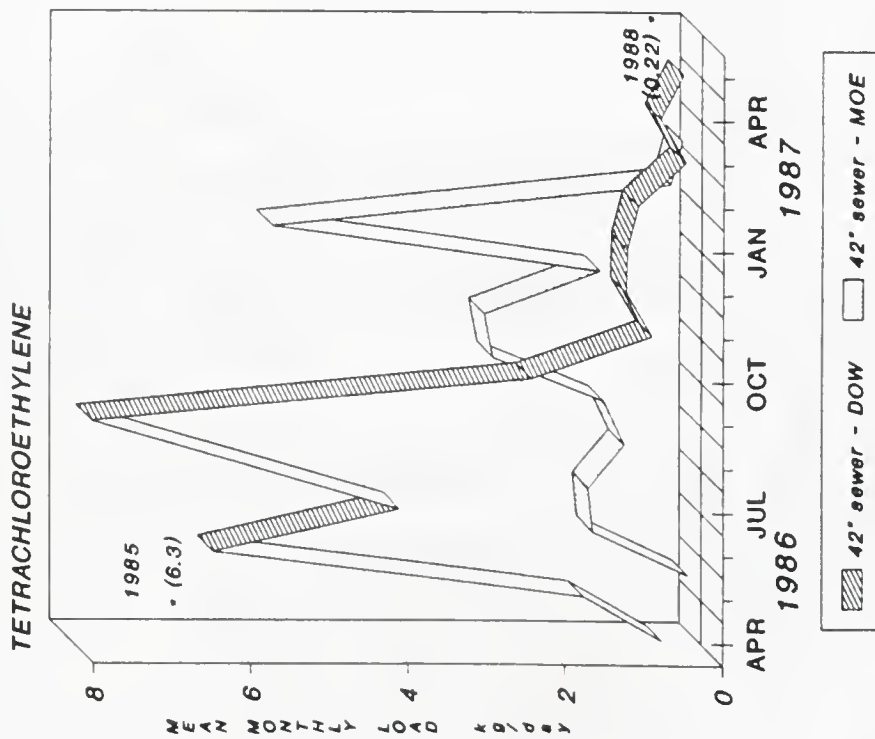


FIGURE 4.1.17: WEEKLY EFFLUENT LOADINGS  
EXPRESSED ON A MONTHLY BASIS



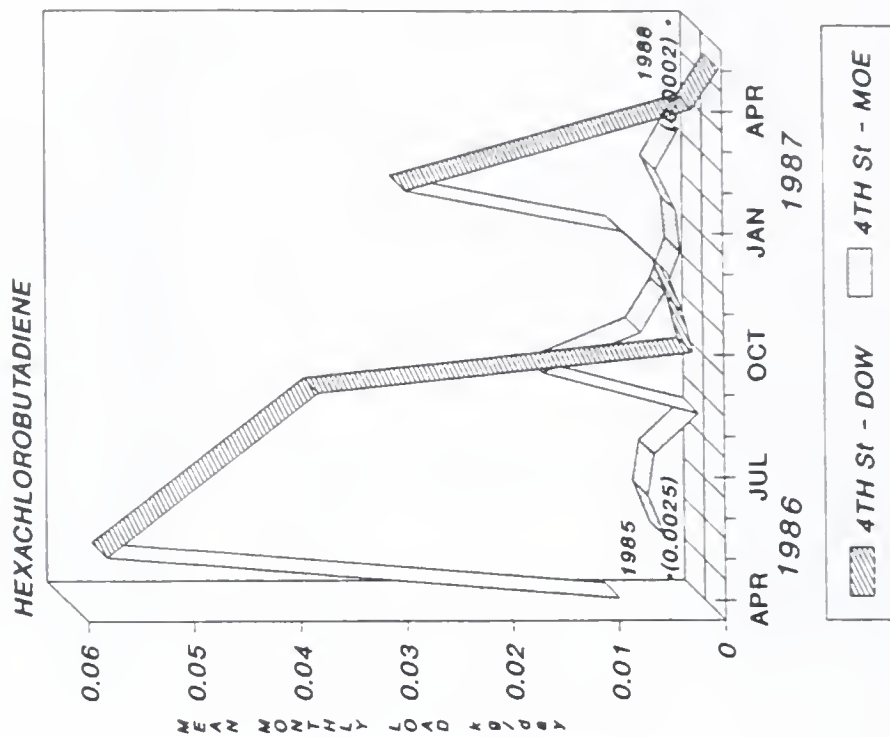
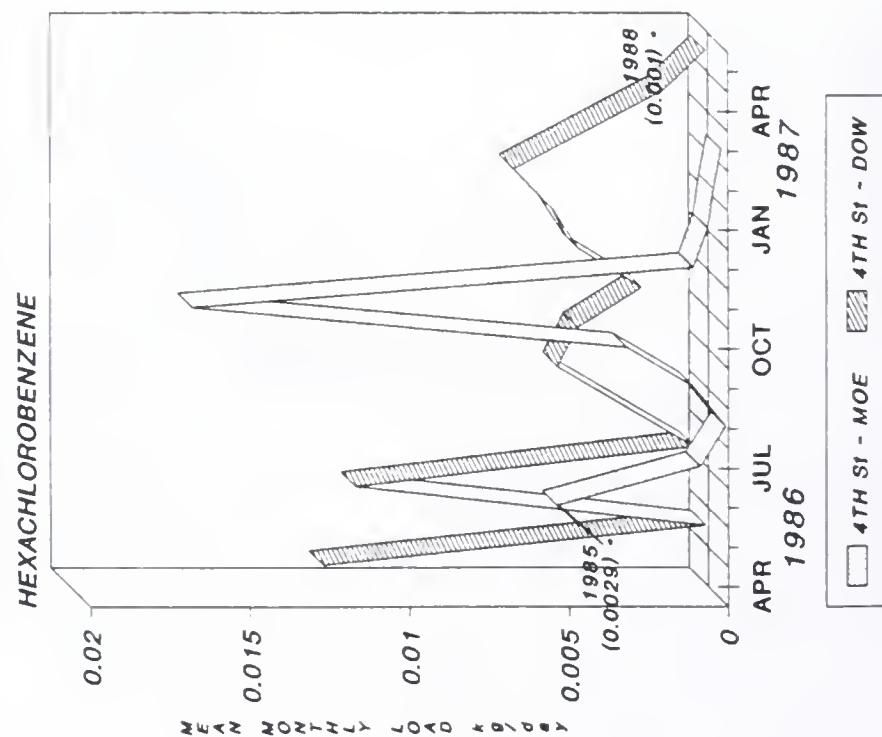
DOW: self-monitoring data  
MOE: long-term effluent monitoring

FIGURE 4.1.18: WEEKLY EFFLUENT LOADINGS  
EXPRESSED ON A MONTHLY BASIS



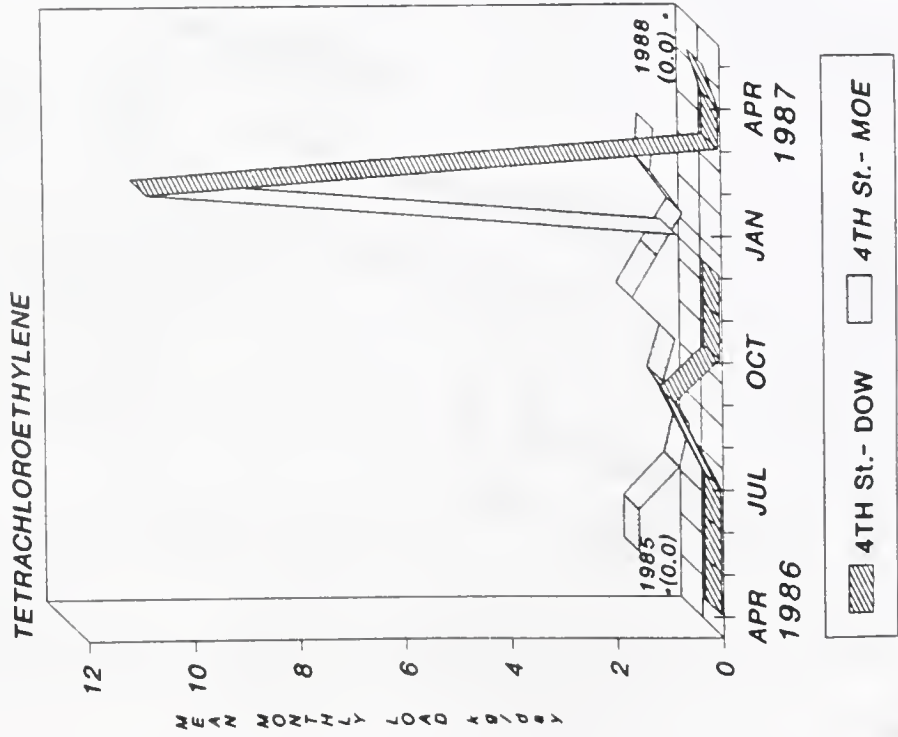
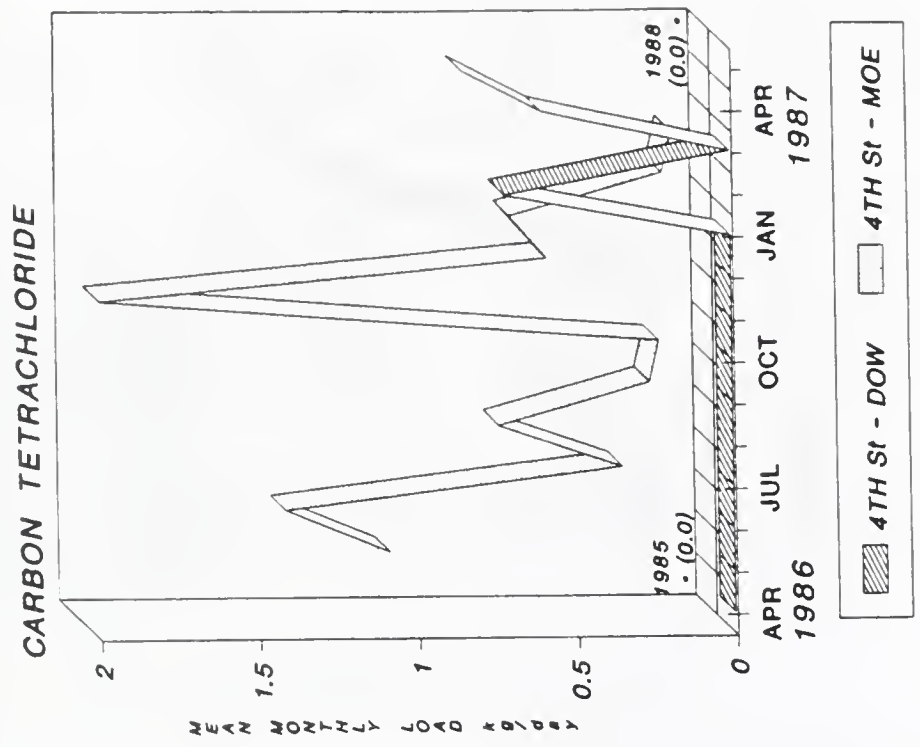
DOW: self-monitoring data  
MOE: long-term effluent monitoring

FIGURE 4.1.19: WEEKLY EFFLUENT LOADINGS  
EXPRESSED ON A MONTHLY BASIS



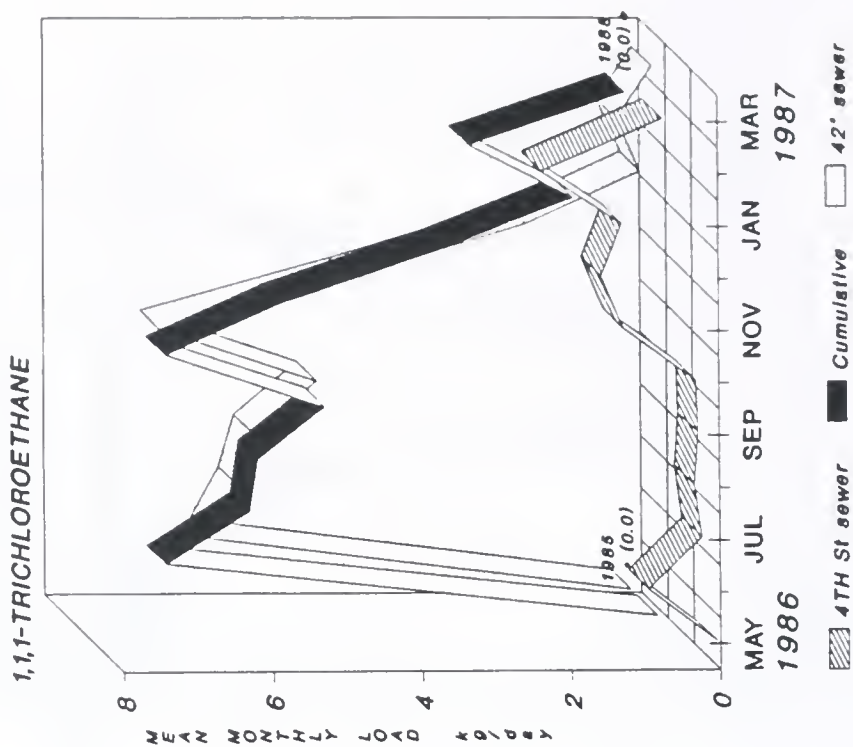
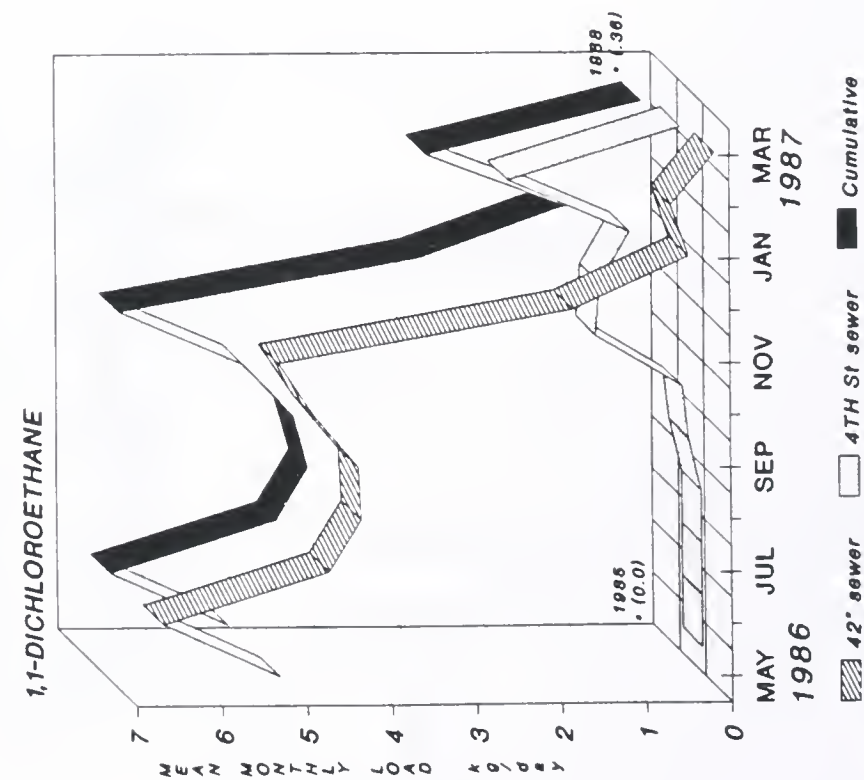
DOW: self-monitoring data  
MOE: long-term effluent monitoring

FIGURE 4.1.20: WEEKLY EFFLUENT LOADINGS  
EXPRESSED ON A MONTHLY BASIS



DOW: self-monitoring data  
MOE: long-term effluent monitoring

FIGURE 4.1.21: WEEKLY EFFLUENT LOADINGS  
EXPRESSED ON A MONTHLY BASIS



A one day intensive survey of Dow sewers was conducted by the MOE during May of 1988 in support of the contaminant fate and transport modelling verification. Sampling efforts were concentrated on the 42-inch and 4th St. sewers (10 samples obtained at 15 minute intervals). Single grab samples were obtained at all other Dow sewers and at Polysar. Loadings are included in Figures 4.1.16 - 4.1.21. In general, loadings measured during May 1988 were extremely low. It is difficult to determine if they are representative of typical conditions particularly in view of the fact that Dow was experiencing a work stoppage (strike) at the time. However, production was maintained by management during this period. More recent Dow self-monitoring data and MOE audit samples, will provide a clearer indication of current contaminant loads from these sewers.

(v) Factors Affecting Contaminant Levels

For outfalls at Dow, shutdowns or interruptions in operation for maintenance or other purposes at specific process plants, do not alter the volume of effluent discharged from sewers.

Typically, even under such circumstances, cooling water (which forms the principle component of sewer discharge) is maintained at operational levels throughout the entire year on a continuous basis (memo from R. Allen, Dow Chemical, to R. Fossburg MOE, Sarnia; August 29, 1988).

As a result, it is anticipated that discharge volumes and contaminant levels would be independent if contaminant concentrations reflect the operational status of process plants. This is observed for most sewers sampled (Figures 4.1.1 to 4.1.7) which have a constant flow regime and contaminant concentrations varying by up to 6 orders of magnitude.

Significance of Groundwater Intrusion vs. Operational Status

It is generally held by Dow that at plants which formulate products and at transfer sites, material spilled historically from handling and



other mishaps on site have contaminated shallow ground water. It is this source of contamination to the St. Clair River which prompted Dow to construct a \$1.3 million slurry wall and collection system along the Dow waterfront.

As a consequence of local spills, tile sewers and those installed below grade are susceptible to intrusion of this groundwater and may reflect contaminants associated with historical spills and not necessarily current operating conditions.

In order to investigate the relationship between contaminant levels and ground water intrusion, a Spearman Rank correlation matrix was assembled for several outfalls (Table 4.1.8). The Cole drain, which experiences hydraulic charges resulting from precipitation, since it receives runoff from the Scott Road ditch catch basin; and the Dow 42-inch sewer which has a constant flow regime of  $60.9 \times 10^3 \text{ m}^3/\text{day} \pm 4.4 \times 10^3 \text{ m}^3/\text{day}$  ( $\pm 7.2 \%$ ) for the period January 1986 to March 1987 (MOE 1988a) were evaluated.

These effluent sampling results are randomly distributed with intermittent impulses or outliers which may greatly influence results of parametric statistical tests such as correlation. The non-parametric Spearman Rank Correlation test is resistant to influence from these peak values and as such, provides an increased measure of confidence vs. parametric comparisons.

The underlying assumption of this comparison is one of increased groundwater intrusion and subsequently elevated contaminant levels coincident with rainfall. If contaminant concentrations do not respond to rain events, the corollary is one whereby they reflect a plants operational status.

The examples which follow do not take into account all factors in making this comparison, and it is expected that further self-monitoring by Dow and MOE audit sampling will provide further insight into the most significant contaminant sources.



A test-wise error rate of 0.05 indicated no significant correlations between precipitation and any of the tested parameters at the 42-inch sewer.

During the sampling period, the 42-inch sewer received cooling water and runoff from the vinyl chloride and propylene oxide plants and cooling water only from the solvents plant.

Cooling water from the vinyl chloride plant has since been re-routed to a newly constructed sewer, while runoff from this area now enters a containment pond and is subsequently recovered.

Contaminants entering the 42-inch sewer from groundwater would likely require some time to enable seepage to occur. In order to account for this effect, precipitation was included for two days prior to sampling and as such, allowed for a period of groundwater intrusion to occur.

At the Cole drain, precipitation was positively correlated with suspended solids and HCB. This likely reflects runoff and/or resuspension of particle-bound contaminants. Materials such as Perc and CCL4 do not appear to preferentially sorb to sediments (see section 4.2.1-centrifugation) and are therefore less susceptible to runoff or resuspension.

Precipitation was significantly correlated with several parameters at the 48-inch sewer, which receives only cooling water from the vinyl chloride monomer and solvent plants, and would be expected to typically incur low levels of contaminants.

These results are only partially consistent with what may be expected to occur. The 42-inch sewer is located below-grade and as such, would be subject to groundwater seepage. While this may be the case, it appears that contaminant levels are more dependent on factors other than this, and likely reflect the operational status of process plants discharging to the outfall.

Findings which support the above statements are presented in Figure 4.1.21 for 1,1-dichloroethane and 1,1,1-trichloroethane. The former is an intermediate product in the manufacture of 1,1,1-trichloroethane produced at the vinyl chloride monomer plant.

Prior to November 1986, process flow from this plant was directed to the 42-inch sewer. From November 6, 1986, process flow from the vinyl plant was redirected to the block 90 pond and subsequently, the 4th Street sewer.

Mean loadings in the 4th Street sewer increased by 441% for 1,1,1-trichloroethane and by 19 fold for 1,1-dichloroethane subsequent to the diversion. This increase may have been partially attributable to batch transfers of groundwater from the slurry wall extraction wells also initiated in the latter part of 1986. However, concurrent reductions of 85% and 66% for 1,1,1-trichloroethane and 1,1-dichloroethane respectively were observed at the 42-inch outfall following the diversion, supporting the conclusion that contaminant levels are not independent of operating conditions. It is important to note that cooling water and runoff water from this plant were still routed to the 42-inch sewer at that time.

A similar diversion implemented in June of 1986 involved separation of solvent plant cooling water from effluent streams. Process, runoff and deluge water were subsequently discharged to the block 90 pond following treatment by steam stripping, while cooling water continued to be discharged to the 42-inch sewer.

It is difficult to determine what, if any changes may have arisen as a result of this diversion since monitoring was initiated in May 1986. Thus, it was not possible to adequately document the "before" conditions with only one month of data.

#### Effects of Block 90 Pond on contaminant levels:

The Block 90 pond is a spill containment reservoir designed to confine accidentally spilled material to within Dow property and prevent losses

TABLE 4.1.8: SPEARMAN RANK CORRELATION RESULTS: COEFFICIENT  
(SIGNIFICANCE)

PRECIPITATION vs:

<u>PARAMETER</u>	<u>COLE DRAIN</u>	<u>42-inch</u>	<u>48-inch</u>
HCB	0.2919 (0.0169)*	0.2222 (0.0649)	0.2642 (0.0271)*
HCBD	0.1376 (0.2635)	0.0371 (0.7599)	0.2718 (0.0240)*
HCE	0.0868 (0.4805)	-0.0648 (0.5956)	0.0137 (0.9092)
OCS	0.0290 (0.8140)	0.0216 (0.8587)	0.0703 (0.5595)
QCB	0.2374 (0.0538)	-0.0206 (0.8653)	0.2840 (0.0183)*
2,4,5-TCT	0.0353 (0.7741)	-0.0669 (0.5812)	0.0644 (0.5928)
CCL4	-0.0711 (0.5755)	0.1798 (0.1636)	-0.1460 (0.2541)
CHLORIDE	0.0876 (0.5198)	0.0648 (0.6338)	0.1725 (0.2009)
PERC	0.1241 (0.3286)	0.0533 (0.6797)	-0.0968 (0.4497)
RSP	0.3525* (0.0042)	0.2133(n=12) (0.4793)	-0.0703(n=20) (0.7591)

\* Significant at test-wise error rate of  $\alpha = 0.05$   
RSP = suspended solids

to the St. Clair River. As indicated previously, this pond receives process streams from a number of facilities within the Dow complex including the solvents plant.

This plant produces chlorinated solvents including tetrachloroethylene and carbon tetrachloride from electrolysis of feedstock hydrocarbons in the presence of excess chlorine (King 1987).

Many of the by-products which occur through the manufacture of chlorine, are extremely hydrophobic. It has been demonstrated that a number of these by-products (HCB, HCE, HCBd and OCS) tend to adsorb to particulate materials in the effluent stream due to their hydrophobic nature (see Section 4.2.1).

Upon entering the Block 90 pond, much of this material would settle to the bottom during the approximately two day retention period. Some other compounds which are more volatile (e.g., perc; CCL<sub>4</sub>) would be lost to the atmosphere.

This type of passive treatment has resulted in further net decreases of contaminant loadings to the St. Clair River from the Dow complex.

An informal study conducted by Dow in November 1987 confirms this finding as volatile organic contaminant levels were reduced by 67% across the pond (inlet concentration compared to outlet concentration) and higher chlorinated compounds such as HCB, HCE and OCS were reduced 80%, 29% and 65% respectively (data provided by R.W. Allen, Dow Chemical Canada Inc.)

Self-monitoring data will provide additional information as to the significance of the Block 90 pond in contaminant removal. Further, this data will enable corrective action to be taken if necessary.

Additional sampling should be conducted to evaluate the significance of the Block 90 pond as a contaminant "sink" with consideration of effects on air quality and depositional sediment quality.

Additional monthly monitoring (July 1986 - June 1987) undertaken by Dow at the outlet of Block 90 pond provides further insight into contaminant interactions. Figure 4.1.22 illustrates trends consistent with reduced volatility during the cold winter months as well as reduced suspended solids for adsorption due to snow cover. The net effect is one of increased contaminant concentrations particularly in the January to April period. These conclusions require further confirmation through continued studies, as they may represent excursions from normal operating conditions.

While this handling of waste streams is not considered a form of treatment, attempts should be made to quantify the atmospheric losses as it is not an acceptable practice to reduce water borne loadings by increasing loadings to the atmosphere.

As a result of the diversion of process water to Block 90 pond, and the subsequent reduction across the pond, losses from the 4th St. sewer were not as high as anticipated. Current loadings are at or above those observed during November 1985 for HCB, HCB<sub>D</sub>, Perc and CCL<sub>4</sub> as well as a number of other parameters (Table 4.1.4). Further to this change was a reduction in contaminants from the 42-inch sewer which now receives primarily once-through cooling water.

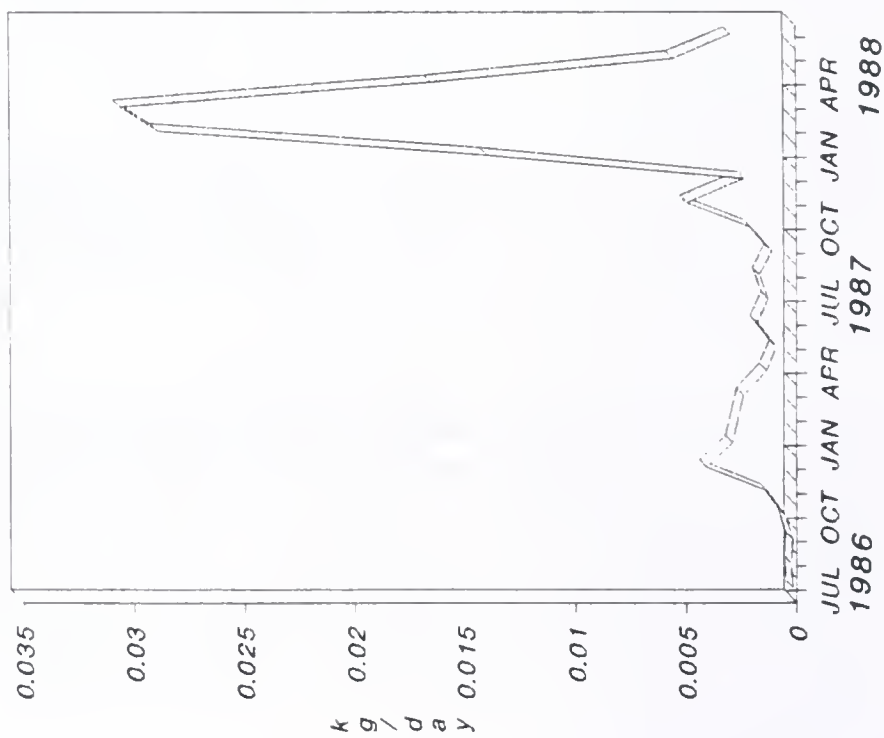
(vi) The Cole Drain

As indicated in Section 2.2.3, the Cole drain is subject to discharges of treated and untreated leachate as well as runoff from a mixed urban/industrial watershed. In addition, industrial effluent and cooling water is discharged to the drain.

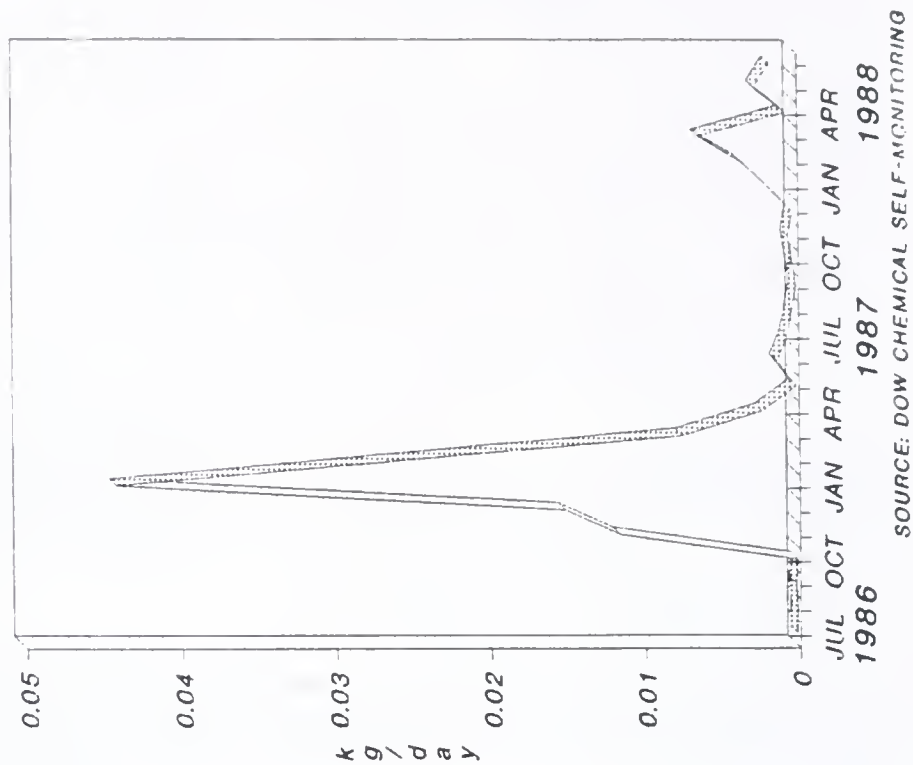
Of concern are operational and decommissioned landfill sites situated adjacent to the Scott Road ditch/drain and the Cole drain. These sites are owned by Polysar, Dow Chemical, Fiberglas, Imperial Oil and the City of Sarnia.

FIGURE 4.1.22 : MONTHLY SUMMARY OF LOADINGS  
AT BLOCK 90 POND OUTLET (kg/day)

# HEXACHLOROBENZENE



# HEXACHLOROETHANE



SOURCE: DOW CHEMICAL SELF-MONITORING



The Dow Scott Road landfill leachate treatment system has been assessed as part of the Upper Great Lakes Connecting Channels Study (UGLCCS) 1989 as well as by Dow Chemical. This latter study determined that the carbon treatment beds would require more frequent re-charging in order to facilitate removal of volatile hydrocarbons.

A 1985 study conducted by Environment Canada evaluated leachate pre- and post-carbon treatment. A number of volatile compounds were detected in the ppm (mg/L) range following treatment, while chlorinated hydrocarbons such as HCB and 1,2,4-trichlorobenzene were quantified in the low ppb ( $\mu\text{g/L}$ ) range.

The removal efficiency of extractable chlorinated compounds by carbon filtration appeared to be much greater than observed for volatile organic compounds.

While the Dow landfill site is a known source of contaminants, other sites are currently under investigation as part of a MOE consultants study of the Cole drain.

Preliminary findings indicate that the Polysar flyash pond may be a source of contaminants; however, seepage from other potential sites, including the Dow disposal site may be responsible for contamination in the vicinity of the flyash pond.

A cursory analysis of contaminant loadings entering the St. Clair River via the Cole drain provides the following conclusions:

- The Polysar biological Oxidation Unit (Biox) which discharges to the Cole drain immediately prior to the St. Clair River appears to be responsible for 69% of all volatiles which enter the drain (1.11 kg/day of 1.6 kg/day).
- Conversely, the Biox unit contributes only 0.4% of the chlorinated aromatic compounds discharged via the Cole drain (0.87 g/day of 202 g/day).



In contrast, the Dow 42-inch sewer discharges approximately 168 g/day total extractable organics. This suggests that active sources in the Cole drain drainage basin must be accounted for and specific remedial measures implemented. It is anticipated that steps towards this goal will be achieved as part of the current MOE consultants study.

#### 4.1.2 Centrifugation of Whole Effluent

Additional chemical characterization was undertaken on centrifuged solid material removed from suspension in effluent streams. Solids obtained from a number of effluent streams were subjected to volatile and extractable scans by capillary Gas Chromatography/Mass Spectrometry. This analysis revealed the presence of several compounds either not detected or not listed on the original group of target compounds identified in Table 4.1.1.

Twenty-one compounds were identified and/or quantified by GC/MS on suspended material from the Dow 42-inch sewer. A number of these were not evident following analysis of whole effluent, in particular: dimethyl disulphide; dimethyl sulphide; dimethyl trisulphide; hexachlorobutene; pentachlorobutadiene; pentachlorocyclopropane; tetrachlorobutadiene and tetrafluorobromochloropropane (Appendix 2). The analysis of suspended material permits the quantification of materials likely to occur below method detection limits in whole effluent. Several measured compounds are included on a list of parameters expected to occur in effluent from the solvents plant, based on known chemical processes in the production of chlorinated solvents (see below), highlighting the need for characterization of effluents.

Chlorinated methanes (all isomers)  
Chlorinated ethanes (all isomers)  
Chlorinated propanes and higher alkanes  
Chlorinated ethylenes (all isomers including 'perc')  
Chlorinated benzenes, toluenes, styrenes, xylenes  
Chlorinated butadienes (all isomers)

Vinyl chloride  
Sodium hydroxide  
Sulphuric acid  
Sodium sulphite  
Sodium hypochlorite  
Ethylene glycol  
Diphenyl oxide  
Polychlorinated biphenyls (PCB's)  
Polychlorinated diphenylethers (PCDE's)

Source: from King 1987.

A detailed description of methods, results and discussion of centrifuged effluent is presented in Section 4.2.1 with results from ambient centrifuging.

#### 4.1.3 Sequential Sampling - Calibration and Testing of the WASTOX Model

##### (a) Introduction and Purpose

A further effluent monitoring initiative was undertaken to address the effects of discharges from Dow Chemical, the Cole drain and the Polysar 72-inch sewer on the aquatic environment in the vicinity of the Ontario shoreline. Effluent and receiving water samples were collected at 30 minute intervals for a 7 hour period on 3 occasions during 1986. This "Sequential sampling" generated data for use in nearfield calibration and validation of chemical dispersion and fate models.

This frequent sampling over a short duration enabled a "snapshot" of cause-effect relationships to be viewed, such that river station samples were taken from the same water mass to which the outfalls had contributed.

The purpose of this investigation was to collect sufficient data to calibrate, verify and check one or more fate and transport models for subsequent use in predicting the impacts of various loading scenarios on the aquatic environment.

The following four models were investigated during the modelling portion of the study:

- i) WASTOX
- ii) TOXIWASP
- iii) KETOX
- iv) Thomann's Generic Foodchain

(b) Model Description

(i) WASTOX Exposure and Foodchain Model

WASTOX (Water Quality Analysis Simulaton for Toxics) which was developed by Dr. J.P. Connolly of Manhattan College, New York, consists of two models:

- the **dynamic exposure concentration model** which simulates the transport, transfer, and reaction of toxic chemicals in water bodies;
- the **food chain model** which determines the effects of toxic pollutants on individual species and communities of organisms.

The main mechanisms which determine the fate of the pollutant in a water system are:

- **transport**, the physical movement of the chemical caused by the advective movement of water, mixing, scouring, and deposition of solids;

- **transfer**, the movement of the chemical between the air, water and solid phases. It includes volatilization and adsorption;
- **reaction**, the transformation of the chemical. It includes biodegradation, photolysis, hydrolysis and oxidation.

The WASTOX model includes a generalized unsteady food chain which incorporates data concerning:

- various predator-prey relationships;
- age differentiation within species;
- migration of species;
- biological activity including respiration and growth;
- assimilation and bioaccumulation;
- benthic and pelagic species.

#### (ii) TOXIWASP Exposure Model

The TOXIWASP model was selected because it incorporated the advantages of WASP (DiToro et al. 1981) and EXAMS (Burns et al. 1982) and adds the sediment water interaction. Moreover it was proven to be useful for toxic chemicals in the Great Lakes environment (Great Lakes Institute 1986). In addition, the TOXIWASP model was used to check the validity of the results of the WASTOX model.

TOXIWASP includes the main mass transfer mechanisms to account for the interactions between the dissolved chemical both with suspended solids and with stationary sediments in the riverbed. These mechanisms include:

- advection and dispersion of dissolved contaminants;
- settling contributions from point/non-point sources of solids and contaminants into the water;
- volatilization and biological degradation.

Volatilization is a major mechanism by which many dissolved contaminants leave the water column. The TOXIWASP model treats volatilization by the two film concept that is used by its predecessor, EXAMS (Burns et al. 1982).

(iii) KETOX Exposure Model

The KETOX model consists of two components namely, the hydrodynamic and the K-E dispersion subprogramme and the mass transport and fate subprogramme. The programme produces a steady state (not varying with time) solution for the depth-averaged velocities, lateral dispersion coefficients, concentrations of contaminants in the water column, the suspended sediments, the bed sediments, and the response time constants to achieve equilibrium. The input data consists of: river flows, river cross-sections, Mannings n (U.S. Corps of Engineers use "n" to represent the bed friction; a typical value of "n" for the connecting channels of the Great Lakes is in the range 0.023 to 0.026), depth corrections from low river stage, initial velocity distribution, diversions and inflows, outfall loadings and locations, kinetic data for the contaminants, partitioning coefficients, concentrations of suspended solids, concentration of solids in the bed, active bed layer thickness, and initial concentration of the contaminant.

(iv) Thomann Generic Foodchain Model

At the Ministry of the Environment Aquatic Food Chain Modelling Workshop, (MOE 1988b) Dr. R.V. Thomann of Manhattan College proposed a four trophic level generic food chain model. The steady state version of Dr. Thomann's model was used in this study. The trophic levels were distinguished by mass. Phase partitioning was assumed for the first level (phytoplankton) while the other levels were assumed to obtain contaminants from both water and food. It is further assumed that a particular trophic level feeds only on the level immediately

below it. The variables included in the model are:  $K_{ow}$ , lipid fraction at each trophic level, mass of organism at each trophic level, food assimilation efficiency, contaminant assimilation efficiency, growth and respiration constants, and dissolved concentrations in the water. The uptake rate is taken as a function of the efficiency of transfer as given by Thomann (1987a, 1987b). The output of the model is the concentration in the lipid and whole body of the organism.

The exposure concentrations from the steady state KETOX and unsteady WASTOX models were used as input to the Thomann model in order to estimate the possible contaminant levels in fish exposed to water in various locations in the St. Clair River and Lake St. Clair system.

Further details of these models are presented in section 6.2.1 under the discussion of load allocation.

#### (b) Field Methods

Three separate cruises were undertaken on May 21st, July 8th and October 1st, 1986. Shore based intakes/outfalls and receiving water monitoring stations were selected to best demonstrate specific cause/effect relationships. These stations are illustrated in Figures 4.1.23 and 4.1.24.

Sampling was conducted jointly by staff from the MOE Southwestern Region and the Great Lakes Section of the Water Resources Branch. Individuals were stationed at each shore location, to enable simultaneous sampling. Two MOE survey vessels were used to obtain samples from the seven river stations. One vessel operated between stations 203, 204 and 215 while the second vessel operated at stations 211 to 218.

A specially designed stainless steel sampling pole, with stainless steel wire baskets designed to house two sample containers for simultaneous collection, was developed to permit rapid and precise sampling at both river and shore based stations.





FIGURE 4.1.23 SEQUENTIAL SAMPLING INTAKES/OUTFALLS



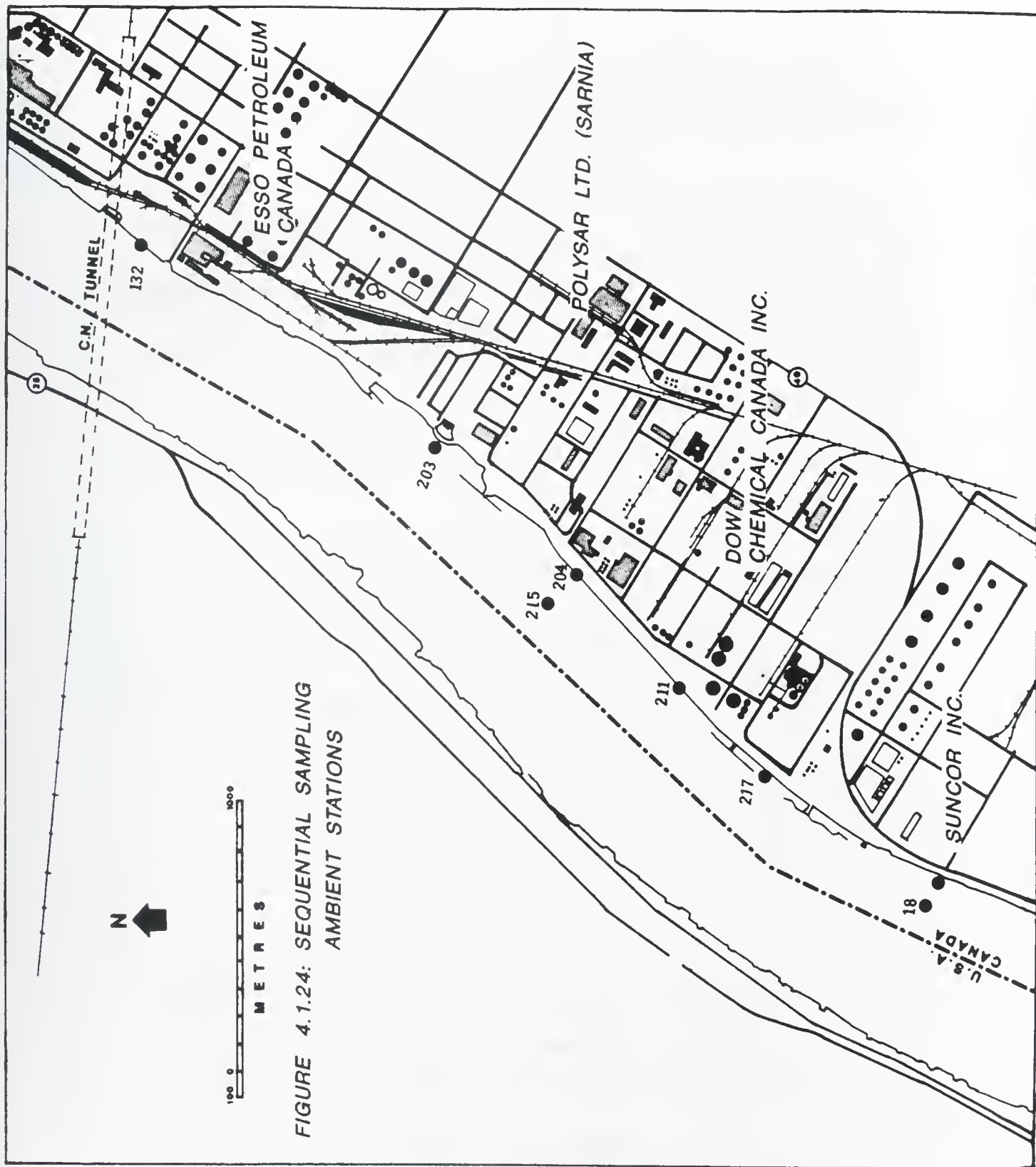


FIGURE 4.1.24: SEQUENTIAL SAMPLING  
AMBIENT STATIONS

Samples were stored in a refrigerated vehicle and transported to the MOE Rexdale laboratory no later than the following morning.

All sampling protocols adhered to MOE guidelines for the collection and submission of samples for laboratory analysis (MOE 1985). Specific field concerns were addressed before sampling through consultation with laboratory staff and a site visit. Volatile samples were air-excluded to eliminate contaminant passage into the head space, and all containers were maintained at 4 degrees celsius prior to analysis.

Samples were analysed for the extensive list of parameters listed in Table 4.1.1.

(i) Modelling Strategy

The data from the three cruises were treated as three sets of independent data. The first set (May 1986 cruise) was used to calibrate the WASTOX exposure model in the vicinity of the outfalls. The half hourly loads were entered as a piece-wise linear forcing function for the five major outfalls. The simulated concentrations for the selected contaminants were compared with the corresponding sequential data. The local dispersion fluxes were adjusted in order to obtain the best possible agreement between model predictions and field data.

The second and third cruises were used to verify the calibration established on the basis of the first cruise. The results of this verification were used to estimate the expected modelling error as a function of the sampling location with respect to the source.

The WASTOX exposure model was selected over two other dynamic exposure models (TOXIWASP and EXAMS) with comparable features in that it also offers the following:

1. It allows for bedload transport in a bottom water segment;
2. It permits up to three sediment sizes to be modelled;
3. There is a food chain submodel available and already compatible with the exposure model.

(ii) River Discretization

For the purposes of modelling, in order to achieve reasonable resolution within the constraints of the model and to maintain tolerable mainframe computing times, it was decided that the river would have to be treated in two reaches. Figure 4.1.25 shows the extent of the fine and coarse grid reaches in the St. Clair River for the WASTOX model.

1. The "fine grid", (see Figures 4.1.26 and 4.1.27 for the upper part of the river (from Upstream of Dow Chemical to Stag Island). Due to the heavy industrialization of the area, finer segments were used to model higher concentration gradients;
2. the "coarse grid" for the lower reach (from Stag Island to Lake St. Clair as shown in Figure 4.1.28). Since this reach contains only a few waste inputs, long segments are used. For both reaches, the river flow is divided laterally into four segments, 5%, 21%, 24%, and 50% starting from the Canadian side. The flow distribution in the Delta is given in Figure 4.1.29.

Figure 4.1.26 shows the WASTOX fine grid reach that was used from the outfall sites to Stag Island. This grid had cells that were as small as 300 m long and had a flow through as low as 0.3% of the total river flow. The introduction of lateral cells was also staged to roughly conform to the outer edge of the effluent plumes. This was done to decrease the number of cells and consequently the size of the system of equations that had to be solved. Even with all of these economizing efforts, the CPU time on an IBM 4381 mainframe was approximately 2 minutes per day of simulation. Thus for the simulation of bed response, which could take one year, the CPU times become prohibitively long.

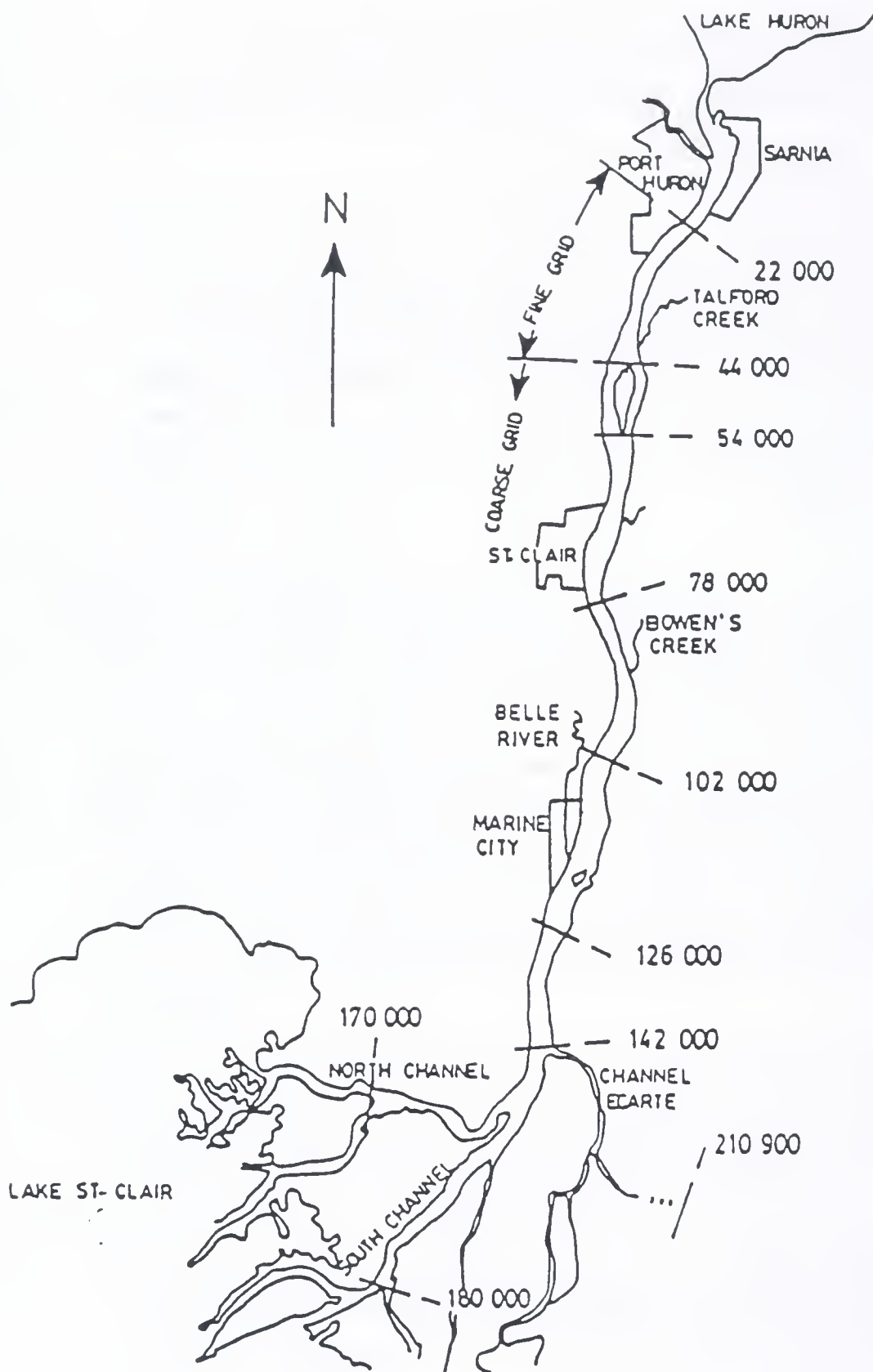


FIGURE 4.1.25: Fine Grid\Coarse Definition for the St. Clair River

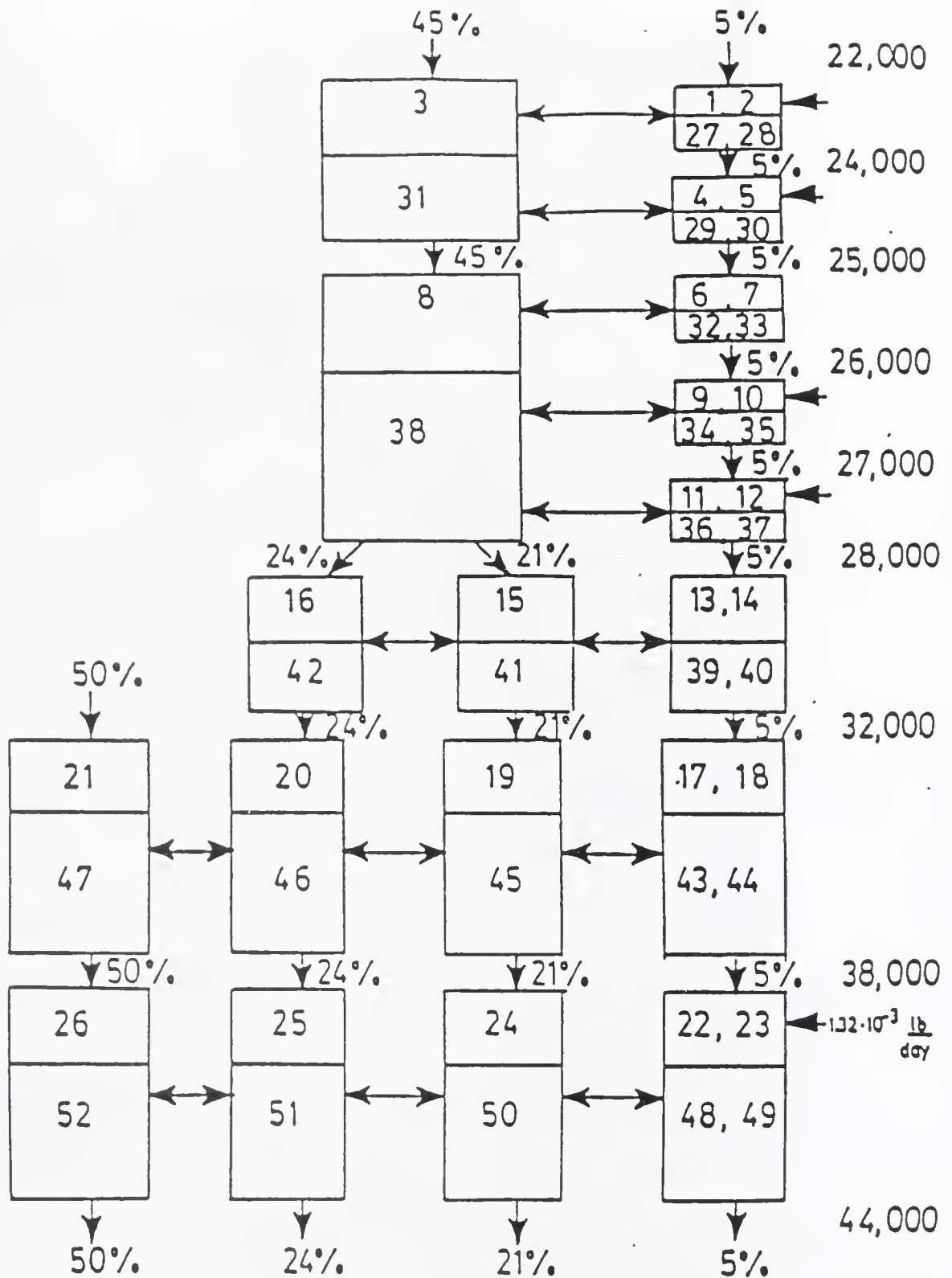


FIGURE 4.1.26: Fine Grid Definition for the the St. Clair River

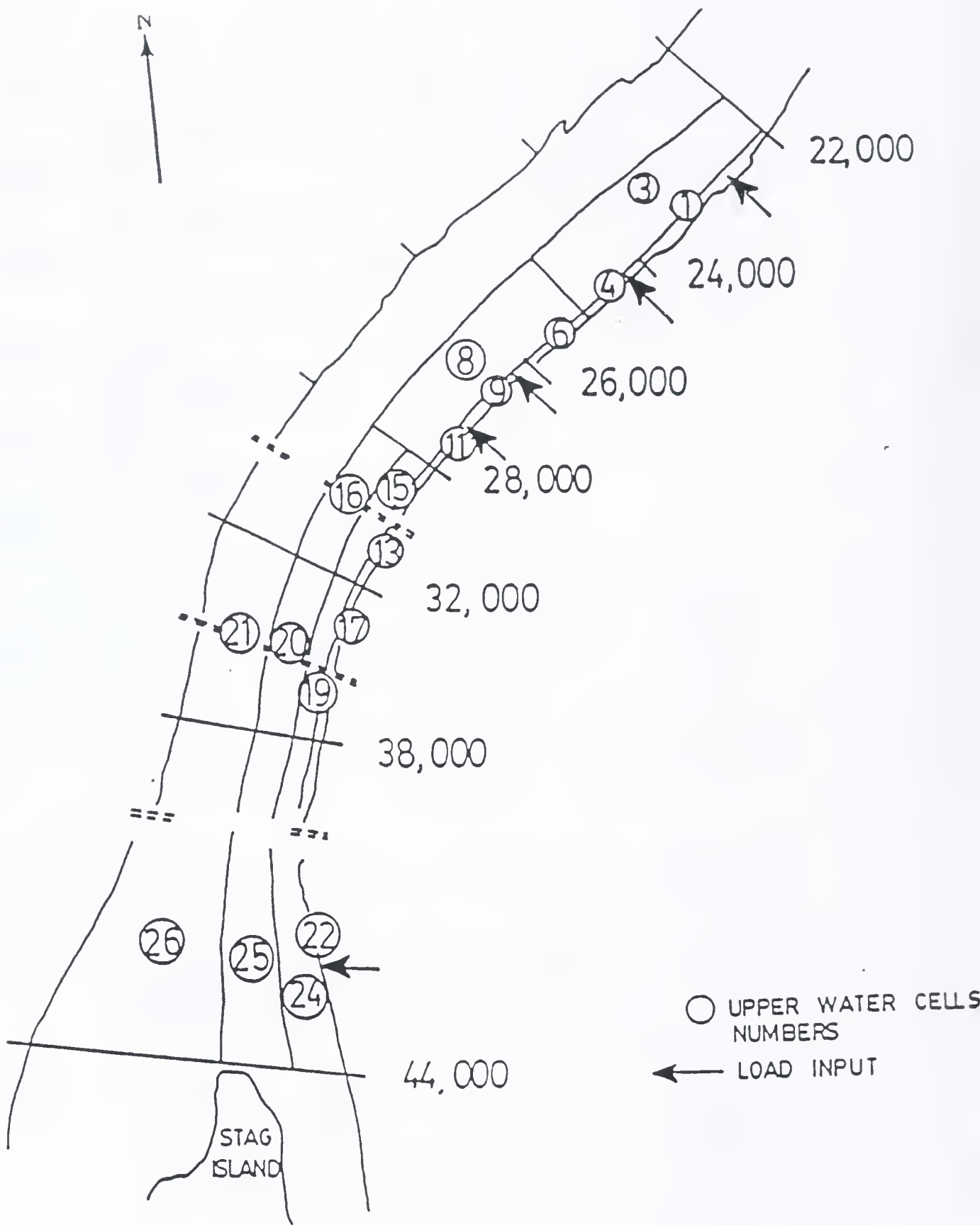


FIGURE 4.1.27: "Fine Grid" Flow Pattern (showing locations of 1985 HCB loads)



The fine grid consisted of active bed cells and a deep bed as well as one or two overlaying water column cells. The two compartment water cells were located adjacent to the Canadian shoreline, i.e. the initial 5% flow tube. At the major outfalls the smaller compartment of the shoreline water column cell was treated as the receiving water for the outfalls. This was necessary to properly represent the size of the initial mixing volume. The outfall discharges are thus initially mixed with river flows of about 11 to 17 m<sup>3</sup>/sec. This yields initial dilutions on the order of 10 to 100 which is within the range of field observations.

The Wastox model may be used with the current fine grid resolution of the St. Clair River, to study spill impacts upstream of Stag Island.

The coarse grid model shown in Figure 4.1.28 was developed for the reach from Stag Island to Lake St. Clair. The shortest cell length in this grid was 1524m which permitted a computation time step which was 5 times that needed for a stable solution in the fine grid model. The downstream output from the fine grid model was used as input to the upstream end of the coarse grid model.

Figure 4.1.30 presents the cross section through these two types of segments. The hydrologic input and dispersion data for both grids was taken from the University of Windsor K-E model.

### (iii) Model Input, Constants and Parameters

Table 4.1.9 summarizes the chemical and physical properties of the selected contaminants that were used for the WASTOX model.

The initial values of the lateral diffusion coefficients in the WASTOX model were obtained from the K-E model. These coefficients were adjusted in the calibration process.

The suspended sediment concentrations and suspended sediment loads were estimated based on the MISA Pilot Site study data as well as data



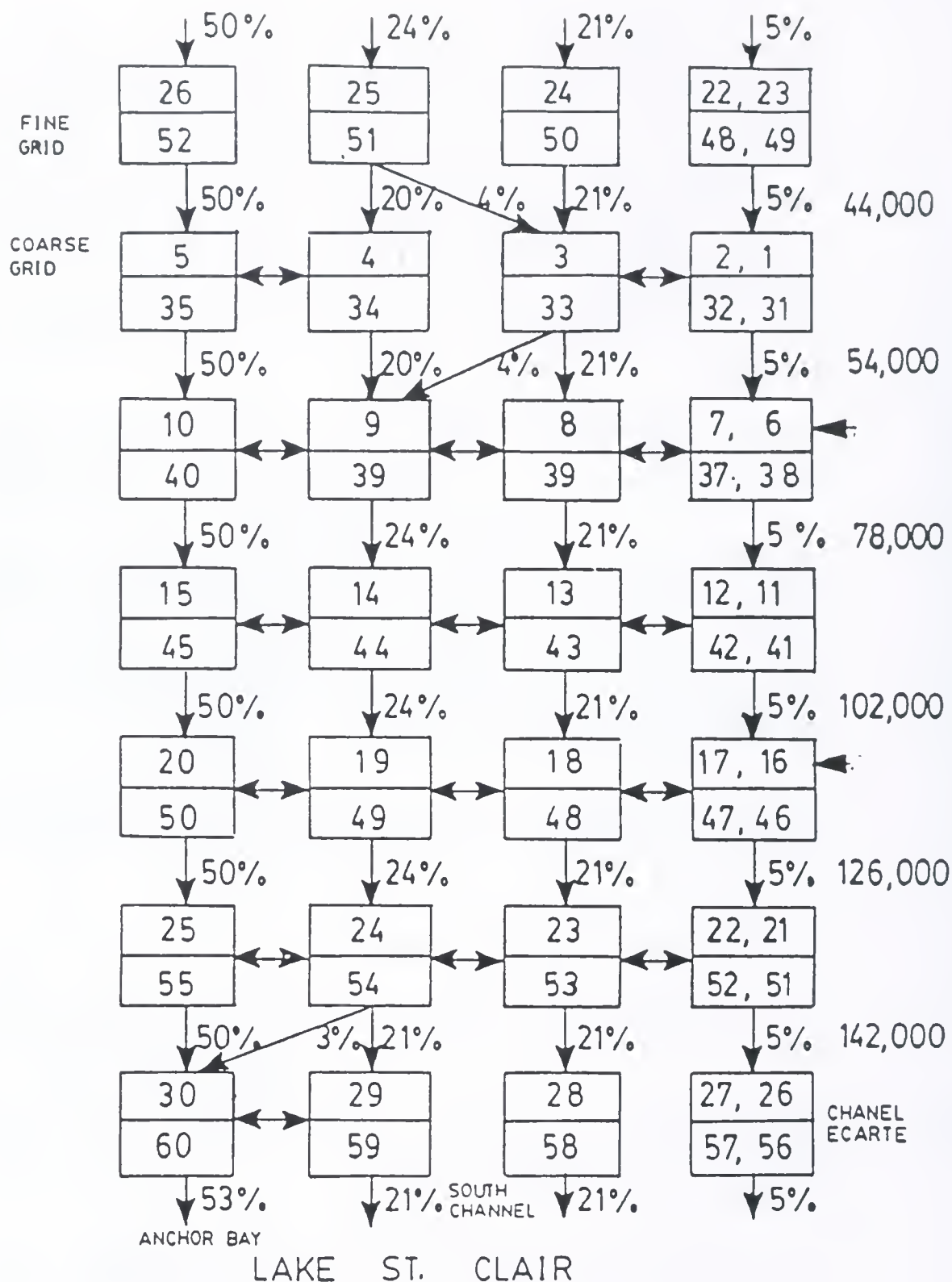


FIGURE 4.1.28: Coarse Grid Cell Definition for the WASTOX Model with 1985 HCB Loads

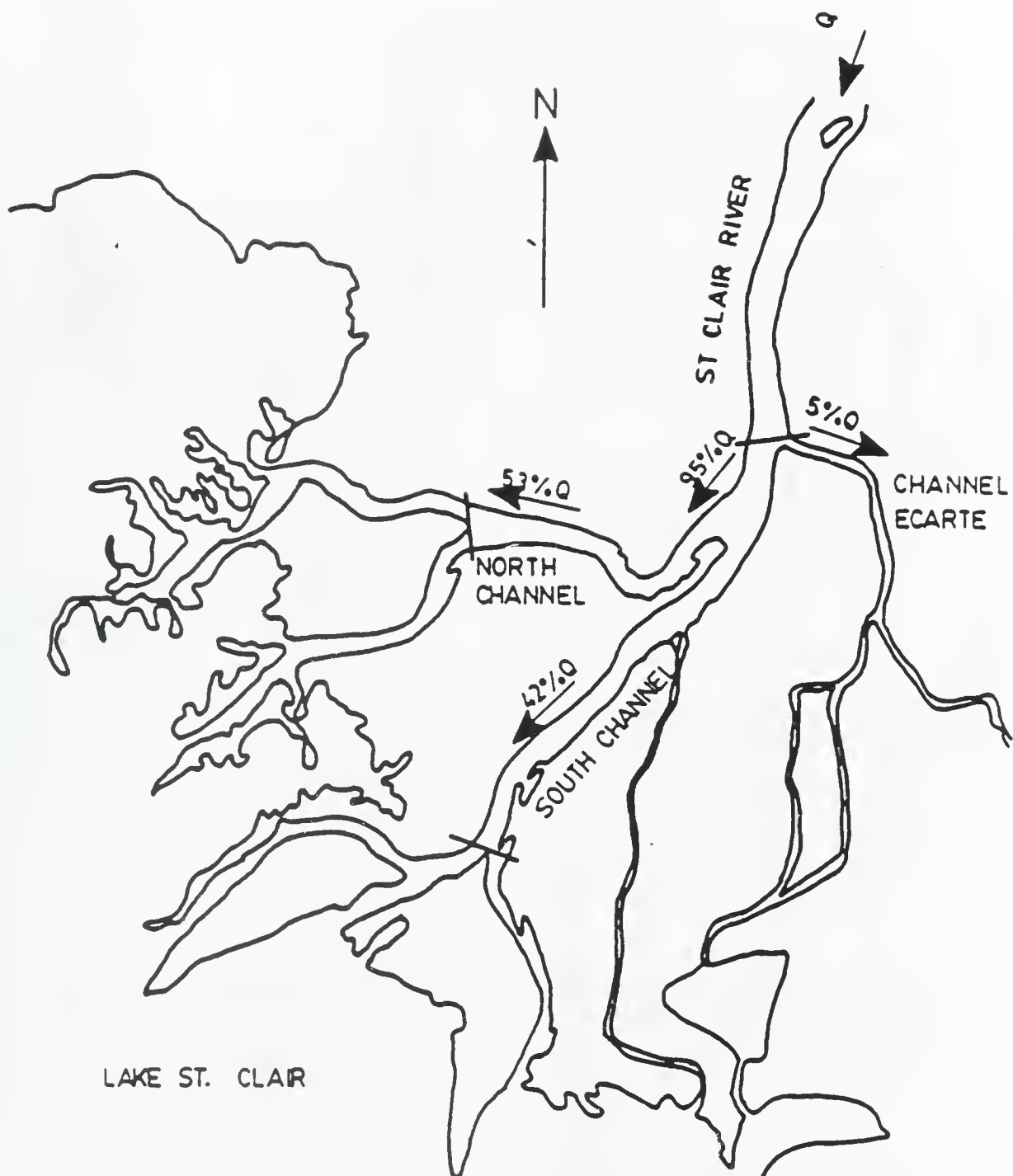


FIGURE 4.1.29: Coarse Grid Flow Distribution in the St. Clair River Delta

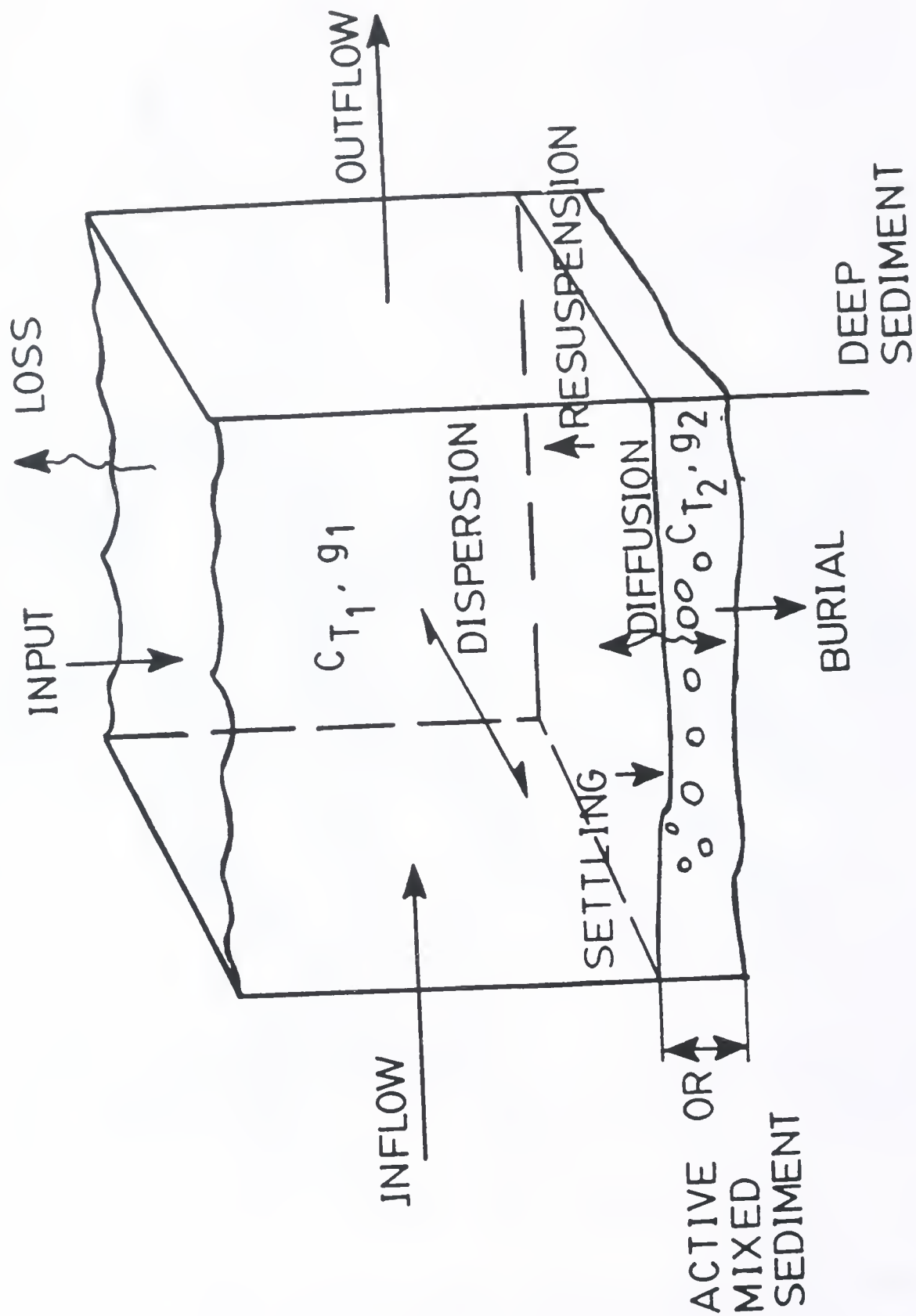


FIGURE 4.1.30: A Typical Cell in WASTOX and TOXIWASP Models

collected for the 1985 spill investigation of the St. Clair River (DOE/MOE 1986). The WASTOX model included three sediment sizes representative of fine (clay and/or biotic material), medium (silt), and coarse (sand and gravel). The MISA data set included information on the size distribution in the river and outfalls.

Similarly, the bed layer was assumed to consist of three sizes of sediment. The 1986 spill report and the 1986 MISA data were used to establish the river bed composition, which varied from hard clay to gravel. The active bed layer was observed to vary from a few centimeters to more than 30 cm.

The estimation of settling rates and resuspension fluxes were part of the initial calibration procedure. The starting values were obtained from the TOXIWASP model that had previously been developed for the UGLCC study (McCorquodale et al. 1986).

#### (c) Results of Field Investigations

For purposes of discussion and model development, a number of selected parameters were examined. To maintain a consistent approach, these parameters are similar to those presented in the long term monitoring section and include HCB, HCB<sub>D</sub>, HCE, PERC and CCL<sub>4</sub>. Data summarized from the three sequential cruises are presented in Appendix 3.

In general, data revealed a fairly random concentration distribution. Many of the compounds analysed were present at concentrations at or below the method detection limits and were therefore unsuitable for model calibration.

A visual interpretation of outfall and receiving water contaminant levels provides several features of interest. Preliminary findings (MOE 1987) have demonstrated a negative correlation in the receiver with increasing distance from shore indicating the rapid lateral gradient which occurs.

TABLE A.1.9: CHEMICAL AND PHYSICAL PROPERTIES OF CONTAMINANTS

CHEMICAL PARAMETERS FOR WASTOX

Constant Variable	DESCRIPTION	UNITS	QCS	HCB	HCB0	HCE	OCL4	PERC
1 KD20	2nd Order biodegradation rate constant for dissolved toxicant at 20 Deg. C	L/d-num (or units compatible with bacterial conc. BACW)	0.	0.	0.	0.	0.	$2.4 \cdot 10^{-1}$
2 KDT	Temp. correction factor for biodegradation of dissolved toxicant		1.	1.	1.	1.	1.	1.
3 KP20	2nd Order biodegradation rate constant for sorbed toxicant at 20 Deg. C	L/d-num (or units compatible with bacterial conc. BACS)	0.	0.	0.	0.	0.	0.
4 KPT	Temp. correction factor for biodegradation of sorbed toxicant		1.	1.	1.	1.	1.	1.
5 KHD20	2nd Order alkaline hydrolysis rate constant at 20 Deg. C	L/role-d	0.	0.	0.	0.	0.	0.
6 KHN20	1st Order neutral hydrolysis rate constant at 20 Deg. C	1/d	0.	0.	0.	0.	0.	0.
7 KHA20	2nd Order acid hydrolysis rate constant at 20 Deg. C	L/role-d	0.	0.	0.	0.	0.	0.
8 KHT	Temp. correction factor for hydrolysis		1.	1.	1.	1.	1.	1.
9 XWSEC	Number of water column segments		26.	26.	26.	26.	26.	26.
10 HENRY	Henry's constant (set to zero to skip volatilization)	Unitless	.173	.208	.208	.208	.832	.636
11 MWLWT	Molecular weight of toxicant		300.	285.	260.8	236.7	153.8	165.8
12 KLT	Temp. corr. factor for volatilization		1.	1.	1.	1.	1.	1.
13 ATWDS	Concentration of chemical in the air (immediately above the water)	microgram/L	$.57 \cdot 10^{-7}$	$3.10^{-6}$	0.	0.	0.	0.
14 IFLOW	Switch to indicate a flowing (0) or non-flowing (1) natural system		0.	0.	0.	0.	0.	0.
15 AIRTEMP	Air Temperature	Degree Celsius	20.	20.	20.	20.	20.	20.
16 A1	Solids dependent partitioning exponent for solids type 1		0.	0.	0.	0.	0.	0.
17 B1	Solids dependent partitioning coefficient for solids type 1	1/mg. (mg.L)	.036	.084	.0315	.000072	.0000075	.000018
18 RH01	Density of solids type 1	gm/ml	2.65	2.65	2.65	2.65	2.65	2.65

In some instances interference was occasionally observed from outfalls which were not nearest to ambient stations. As an example, HCB<sub>D</sub> emitted from the Dow 4th St. sewer was generally at lower concentrations than observed at station 217 located only 15m downstream. In this instance, the effects of the Dow 42-inch sewer with effluent levels 1 to 2 orders of magnitude greater than the 4th St. sewer may be overriding local inputs. This effect would be expected to have diminished subsequent to diversion of solvent plant effluent in June 1986. This was the case during the October (fall) cruise as ambient levels were typically lower than 4th St. sewer levels; however, the distribution at station 217 still appears to mimic 42-inch sewer concentrations (Figures 4.1.31 and 4.1.32).

A similar situation arises for HCB<sub>D</sub> at the Cole drain. Extremely high levels emitted in October 1986 (Figure 3.1.33 and Appendix 3) have resulted in measurable levels at station 215 downstream of the 1st St. Dow sewer complex which is too far offshore to be influenced by these latter outfalls.

HCB measured at station 204 in July 1986 reflects a similar situation. Ambient levels were actually greater than effluent levels from the 42-inch sewer (Figure 4.1.34) . It is possible that an elevated pulse in the effluent was not measured at the 42-inch sewer and/or an upstream source (the Cole drain). These effects in combination or singularly have resulted in the elevated ambient level.

In some instances, a relatively good correlation was observed between effluent and ambient levels. Statistically significant correlations ( $p < 0.05$ ) were demonstrated for HCB at the 42-inch sewer and station 211 in May and July 1986 (Figure 4.1.35).

(d) Results of Model Application

(i) Analysis of Loads

During the sequential study of the St. Clair River, the MOE intensively monitored both discharge and contaminant concentrations at the outfalls



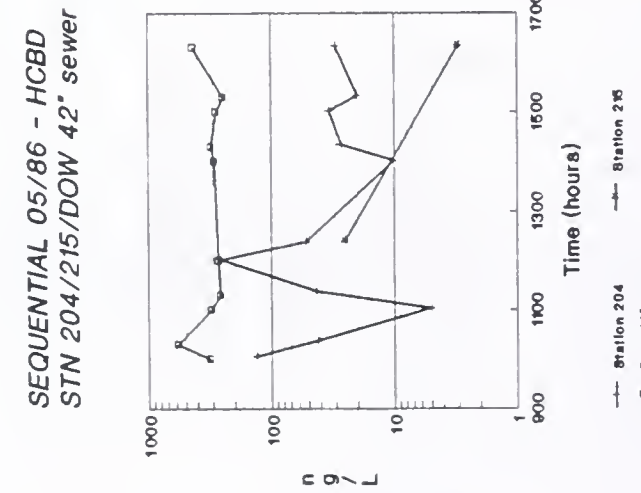
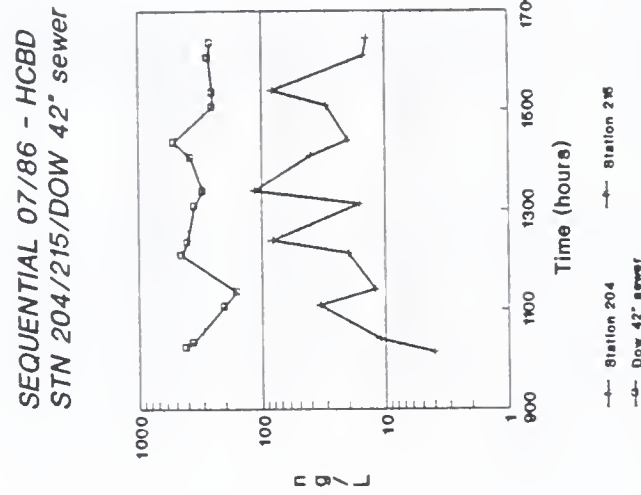
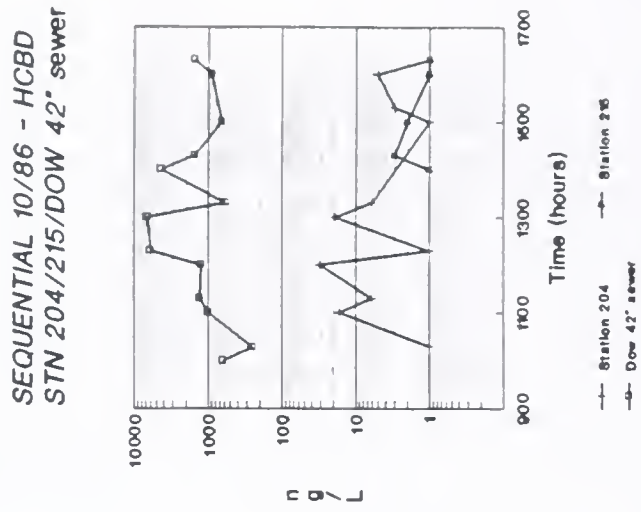
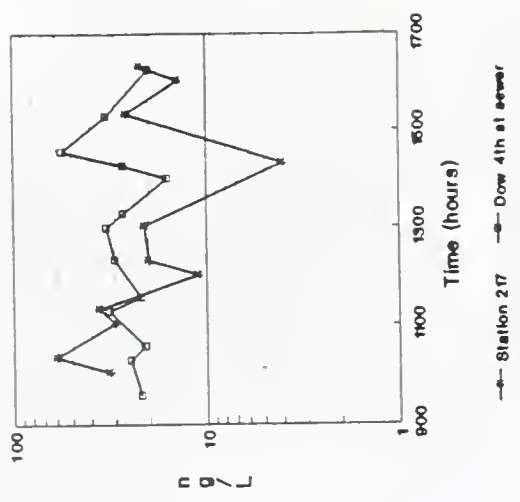


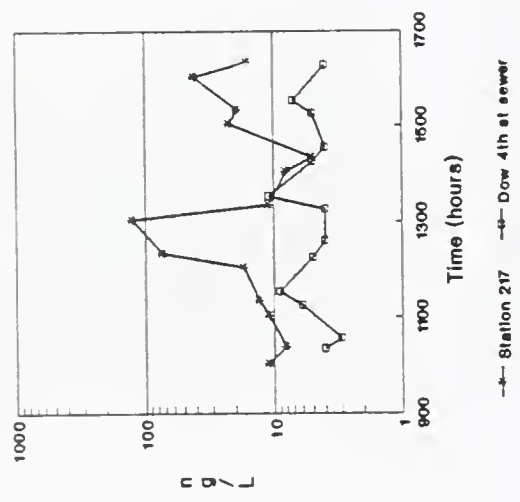
FIGURE 4.1.31 : ST. CLAIR RIVER SEQUENTIAL SAMPLING



SEQUENTIAL 10/86 - HCB  
STN 217/DOW 4TH ST sewer



SEQUENTIAL 07/86 - HCB  
STN 217/DOW 4TH ST sewer



SEQUENTIAL 05/86 - HCB  
STN 217/DOW 4TH ST sewer

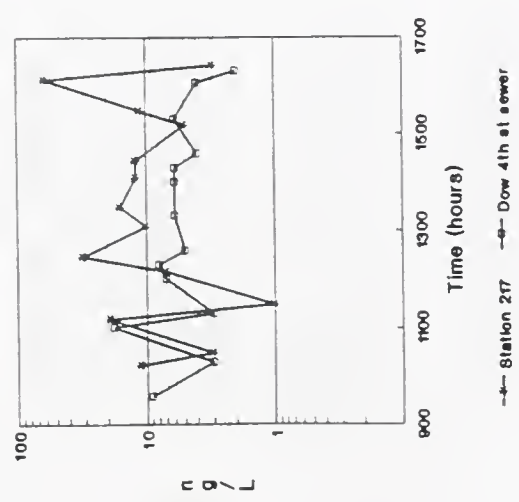
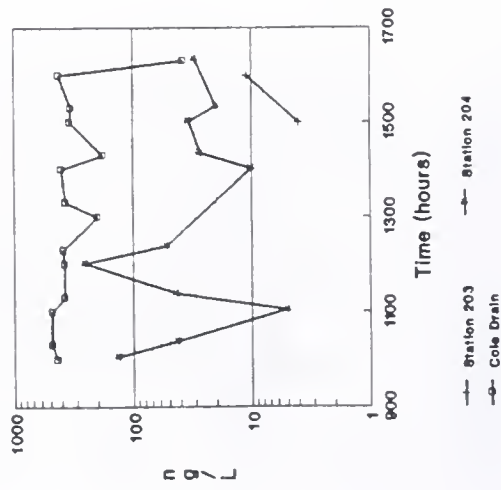
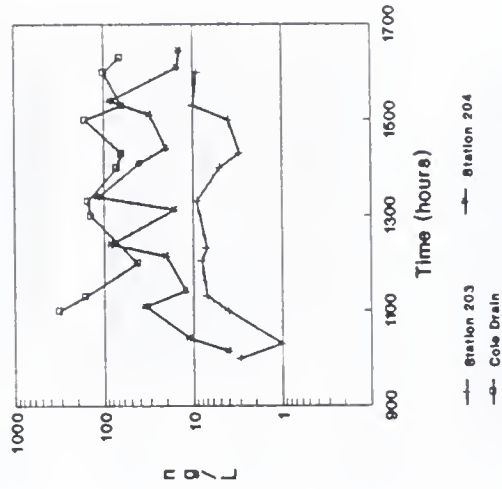


FIGURE 4.1.32 : ST. CLAIR RIVER SEQUENTIAL SAMPLING

SEQUENTIAL 05/86 - HCB  
STN 203/204/COLE DRAIN



SEQUENTIAL 07/86 - HCB  
STN 203/204/COLE DRAIN



SEQUENTIAL 10/86 - HCB  
STN 203/204/COLE DRAIN

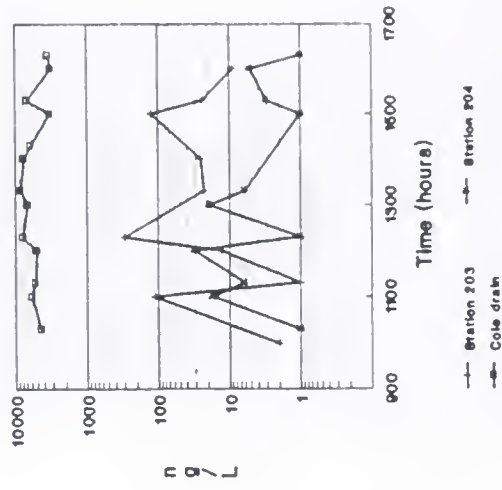
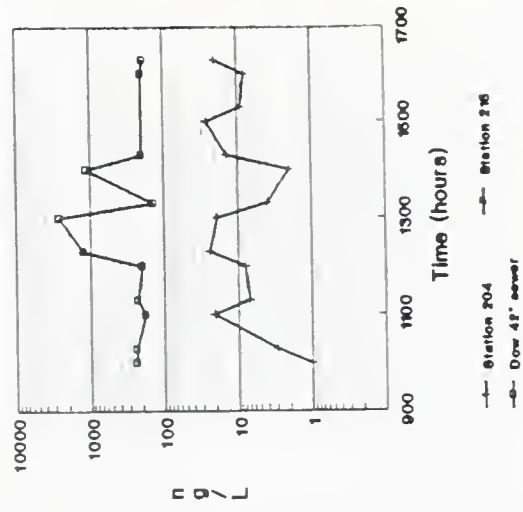
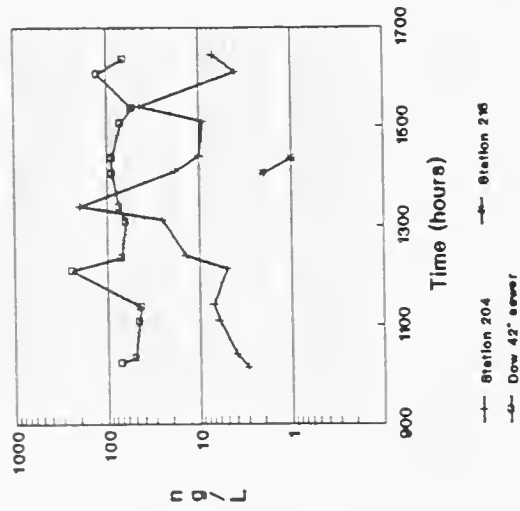


FIGURE 4.1.33 : ST. CLAIR RIVER SEQUENTIAL SAMPLING

SEQUENTIAL 10/86 - HCB  
STN 204/215/DOW 42" sewer



SEQUENTIAL 07/86 - HCB  
STN 204/215/DOW 42" sewer



SEQUENTIAL 05/86 - HCB  
STN 204/215/DOW 42" sewer

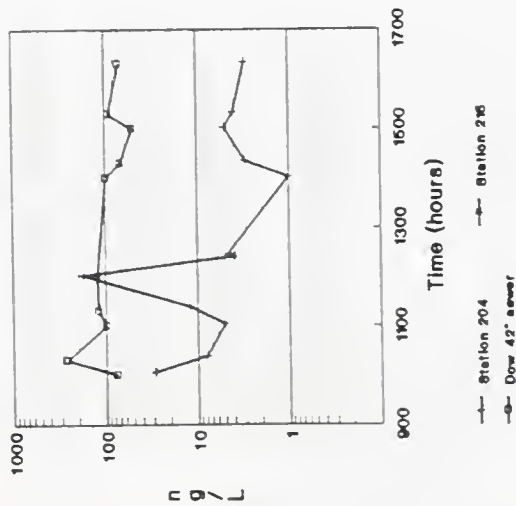
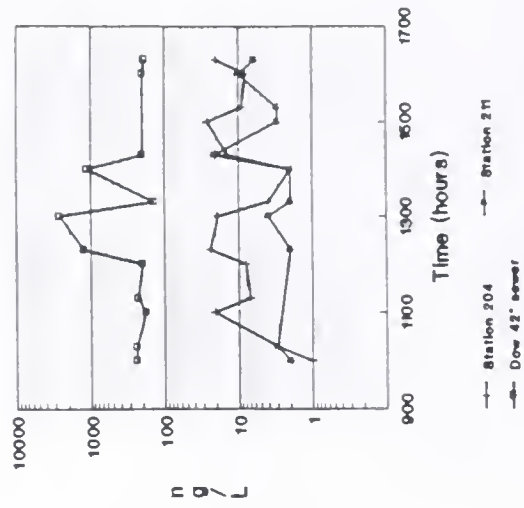
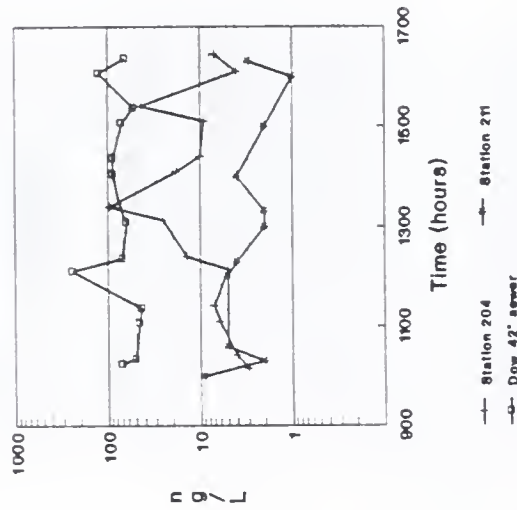


FIGURE 4.1.34 ST. CLAIR RIVER SEQUENTIAL SAMPLING

SEQUENTIAL 10/86 - HCB  
STN 204/211/DOW 42" sewer



SEQUENTIAL 07/86 - HCB  
STN 204/211/DOW 42" sewer



SEQUENTIAL 05/86 - HCB  
STN 204/211/DOW 42" sewer

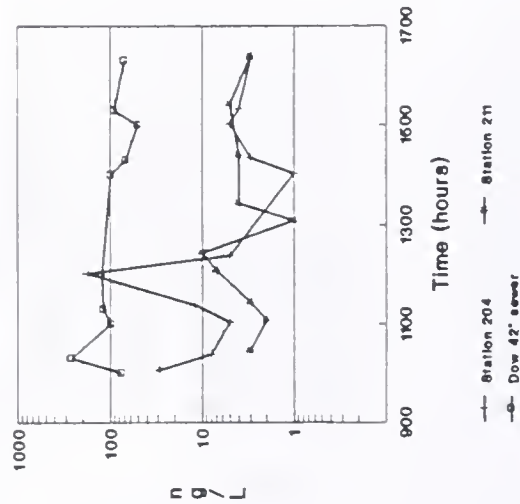


FIGURE 4.1.35 ST. CLAIR RIVER SEQUENTIAL SAMPLING

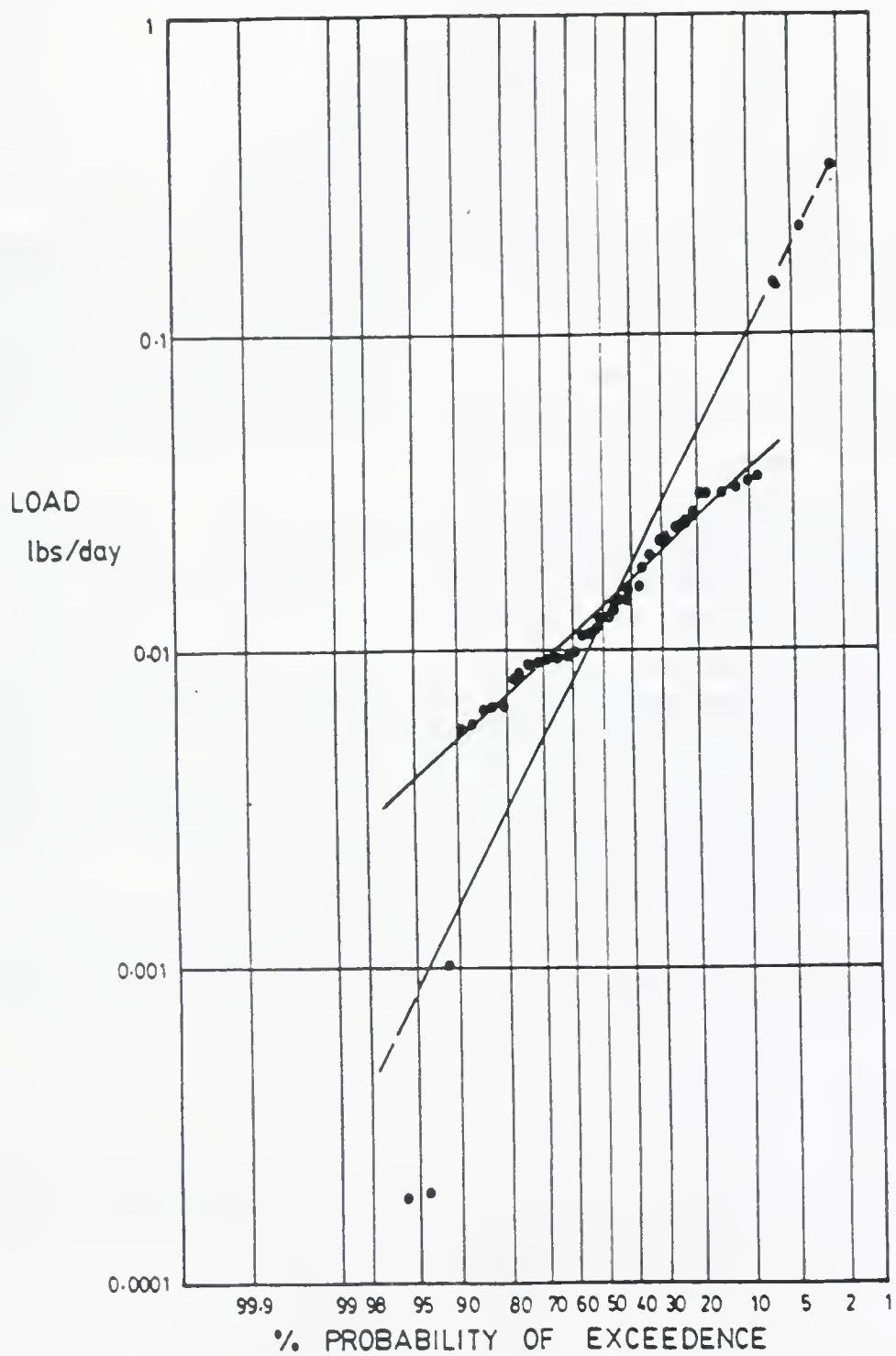


FIGURE 4.1.36: Load Frequency Distribution Curve for HCB for 1986 Sequential Data

listed in Figure 4.1.23. In order to better appreciate the nature of the loads, a statistical analysis was carried out for all of the HCB measurements. This data was plotted on a Log Normal Probability paper as shown in Figure 4.1.36. It is apparent from this figure that most of the data satisfies the Log Normal Distribution. However, there are a few measurements which fall well outside, both higher and lower, than the distribution. These measurements probably represent intermittent pulses of contaminant that occasionally are discharged. Because of the possibly large mass loading associated with these high concentrations, it is important in the modelling process to properly incorporate these extremes into the loading estimates. It is noted that the highest three measurements representing only 6 percent of the total data account for over 50 percent of the loading. In terms of the 7 hour sampling period with half hour intervals, the return period for the extreme readings is  $[0.5/.06 = 8.3 \text{ hours}]$  which is longer than the individual sampling period. The chance of obtaining at least one of the extreme readings in 14 samples is about 58 percent, while the chance of obtaining no spike is 42 percent; thus about 42 percent of the time, the loading would be underestimated by about 50 percent and 32 percent of the time the load would be over-estimated by at least 50 percent due to the implied distribution of spikes. The implication for calibration is that the predicted ambient concentrations should be within + or - 50 percent of the ambient measurements for a 14 point comparison. When the data from all three cruises are combined ( $3 \times 14 = 42$  points or intervals) the risk of 50 percent under or over estimation due to spikes is only 7 percent; thus sampling interval errors will not be very important when all the data are pooled.

#### (ii) WASTOX Calibration

The calibration of the dynamic portion of the WASTOX model was based on the selected five contaminants and the May cruise. The data from the other cruises were reserved for verification.

Two validation checks were applied to the measured data before it was adopted for calibration purposes. First the ambient sequential concentrations were compared with the highest measured concentrations

in the outfall. If the outfall concentrations were lower than the ambient concentrations it was assumed that this data set would not give a reliable calibration; these data were then set aside for verification purposes. Secondly, the KETOX model was used along with the indicated average loadings and the ambient concentrations at the downstream boundary of the sequential study in order to check the mass balance. If less than half of the mass indicated by the product of the measured ambient concentration and the flow distribution computed by KETOX, could be accounted for by the upstream load, then this data set was not used in the calibration.

Sequential data for the May cruise for HCB, HCE, HCB<sub>D</sub>, PERC and CCL<sub>4</sub> in the major outfalls when compared with sequentially measured corresponding ambient concentrations indicated possible correlations that would permit the use of the parameters HCB and HCE for calibration purposes. An anomaly between the measured outfall concentration of HCB<sub>D</sub> and the corresponding ambient concentration made it impossible to use this parameter for calibration purposes. In particular, the ambient concentrations were generally higher than the outfall concentrations. There are several logical explanations for this apparent anomaly, for example: the one-half hour sampling interval may have missed a pulse of HCB<sub>D</sub> and therefore, the sampling may have been biased toward the lower concentration zone; there may have been a buoyant plume resulting in higher surface concentrations in the river. A similar problem arose with PERC and CCL<sub>4</sub>. A mass balance using the ambient measurements (using the KETOX model) indicated that on average the outfall measurements accounted for only 1/3 to 1/2 of the loads. It was therefore not possible to use PERC and CCL<sub>4</sub> in the calibration procedure. It is quite possible that PERC and CCL<sub>4</sub> were transported along the bottom of the pipe, making it difficult to measure. A buoyant plume may have mixed and lifted some of this contaminant in the river water column.



The calibration process involved running the WASTOX fine grid model with the piecewise linear representation of the outfall loads; while adjusting the dispersion exchange fluxes until a reasonable simulation of the ambient measurements were achieved. It was necessary in the calibration process to convert the bottom water cell to a combination bottom and near shore cell in order to properly represent the coupling of the near and far fields of the outfalls. Very low dispersion coefficients were determined for these cells. The fraction of the total flow passing through these cells was on the order of 0.3% of the total river flow.

In order to determine the model's performance, the predicted and measured concentrations of HCB and HCE were compared at all of the measurement sites. These corresponded to cell 5, 10, 12, and 18. Examples for segment 10 are shown in Figures 4.1.39 and 4.1.40 for HCB and HCE respectively.

It was noted that the general level of response of the model was in agreement with the ambient measurements. But both the measured and ambient responses had large and possibly random fluctuations. The fluctuations in the predicted concentrations were directly proportional to those in the measured loads. The predicted concentrations were generally within 1 measured standard deviation of the measured concentrations.

A paired student "t" test was carried out to determine whether a statistical difference between the measured and the predicted mean concentration in the sampled cells existed. These results are summarized in Table 4.1.10. When individual cells were considered for HCB and HCE, a significant difference between the predicted and measured means was observed in 3 out of 8 comparisons. However, when all 8 cases were pooled, an average  $t = + 0.47$  indicated that the measured data sets were slightly higher than the predicted. Figure 4.1.37 shows the measured to predicted concentration ratio for HCB and HCE for cells 5, 10, 12 and 18, for all three cruises; the 10

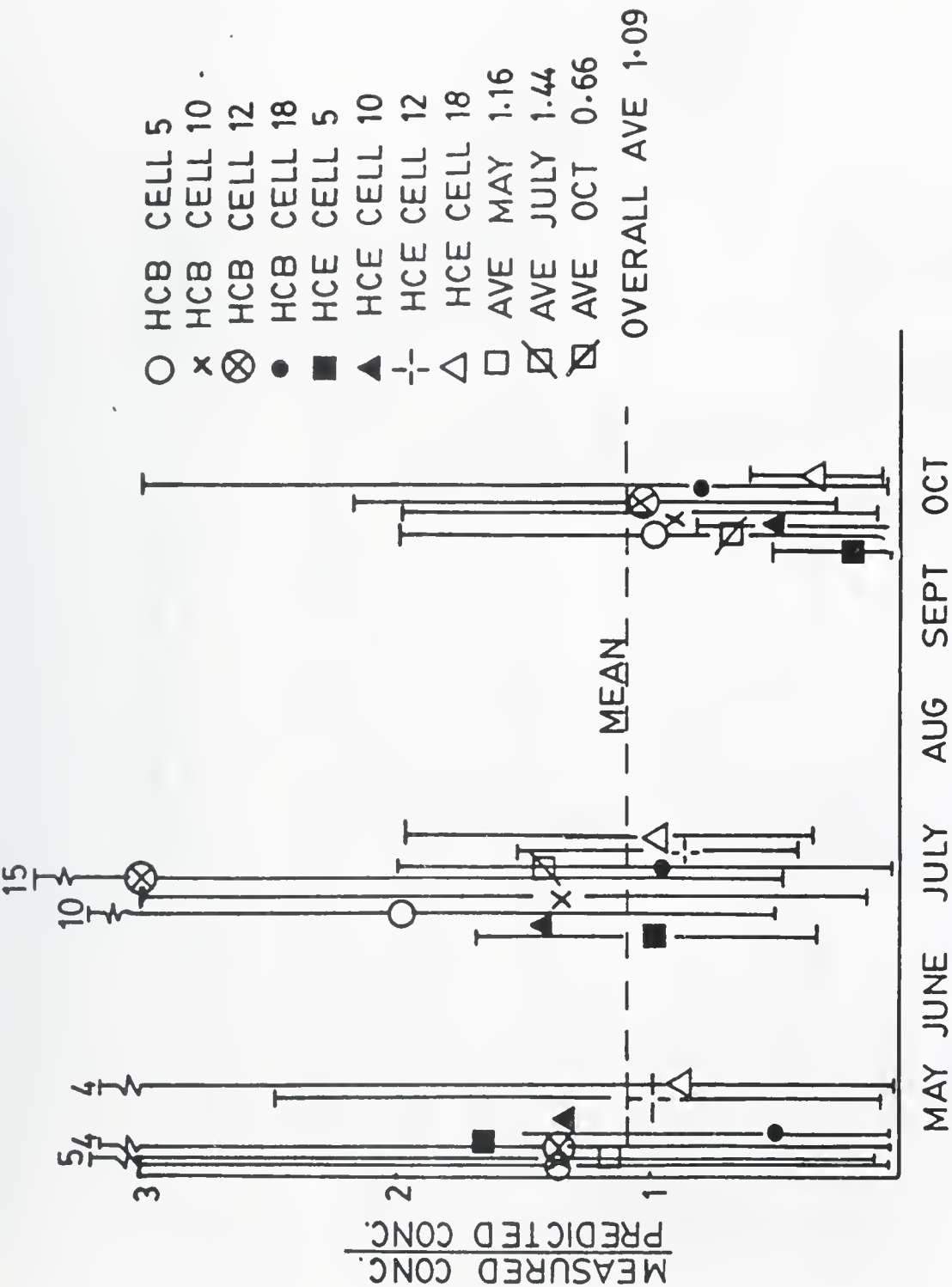


FIGURE 4.1.37: Comparison of Ratios of the Measured to the Predicted Concentrations for HCB and HCE for Cells 5, 10, 12 and 18 for the Spring, Summer and Fall Cruises

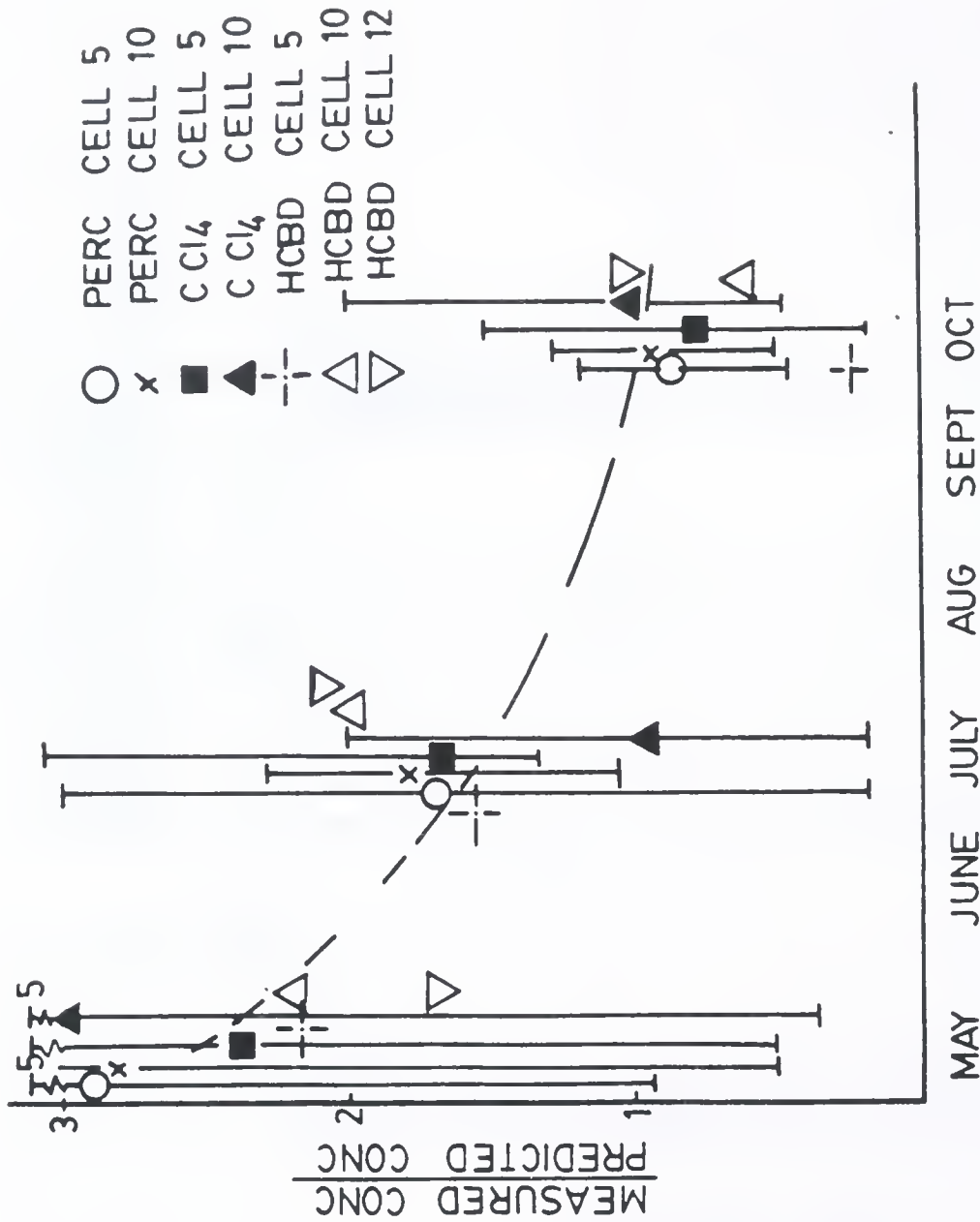


FIGURE 4.1.38: Comparison of the Ratios of the Measured to the Predicted Concentrations for PERC, Carbon Tetrachloride and HCBd

FIGURE 4.1.39: St. Clair River - WASTOX - Fine Grid  
HCB Concentration in Spring

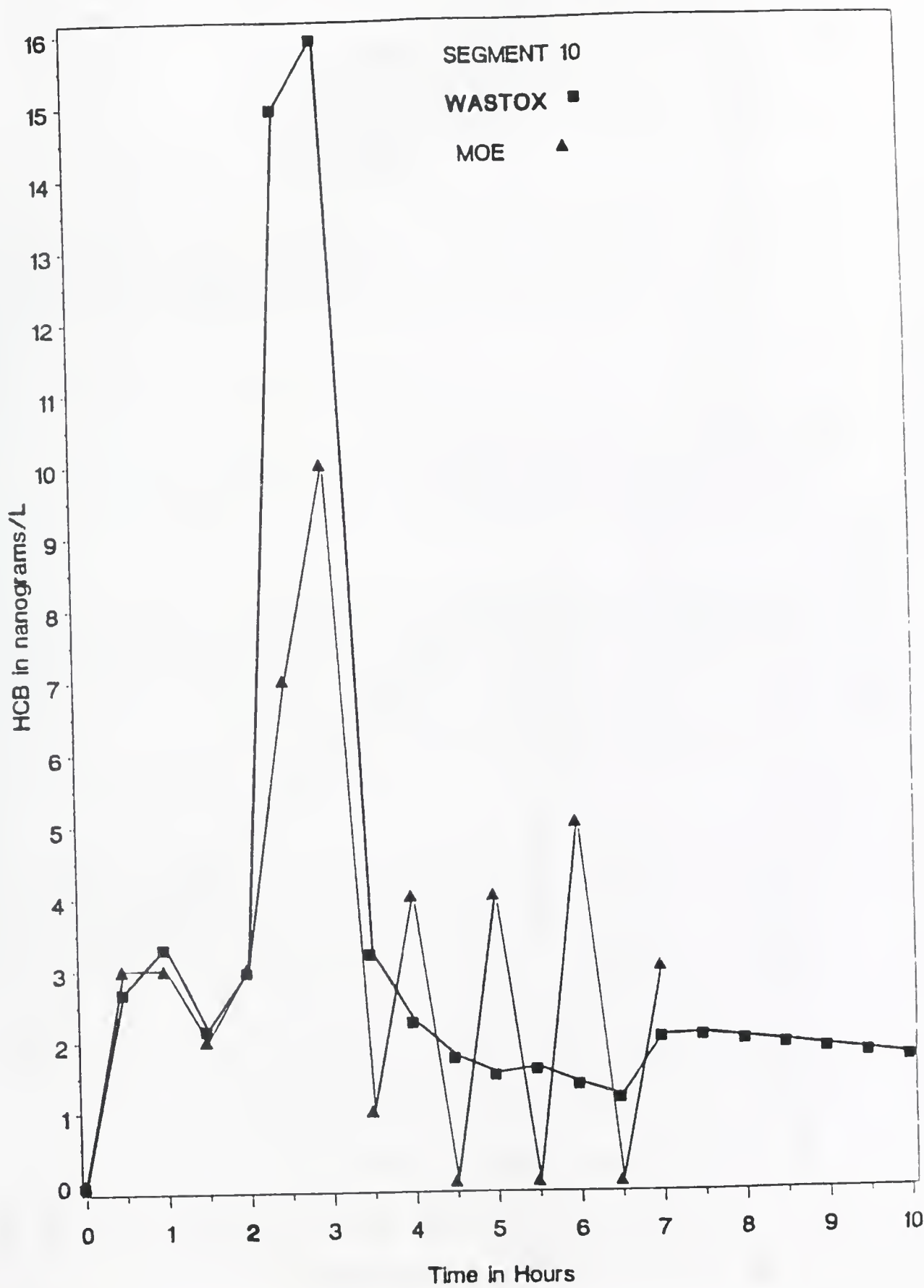
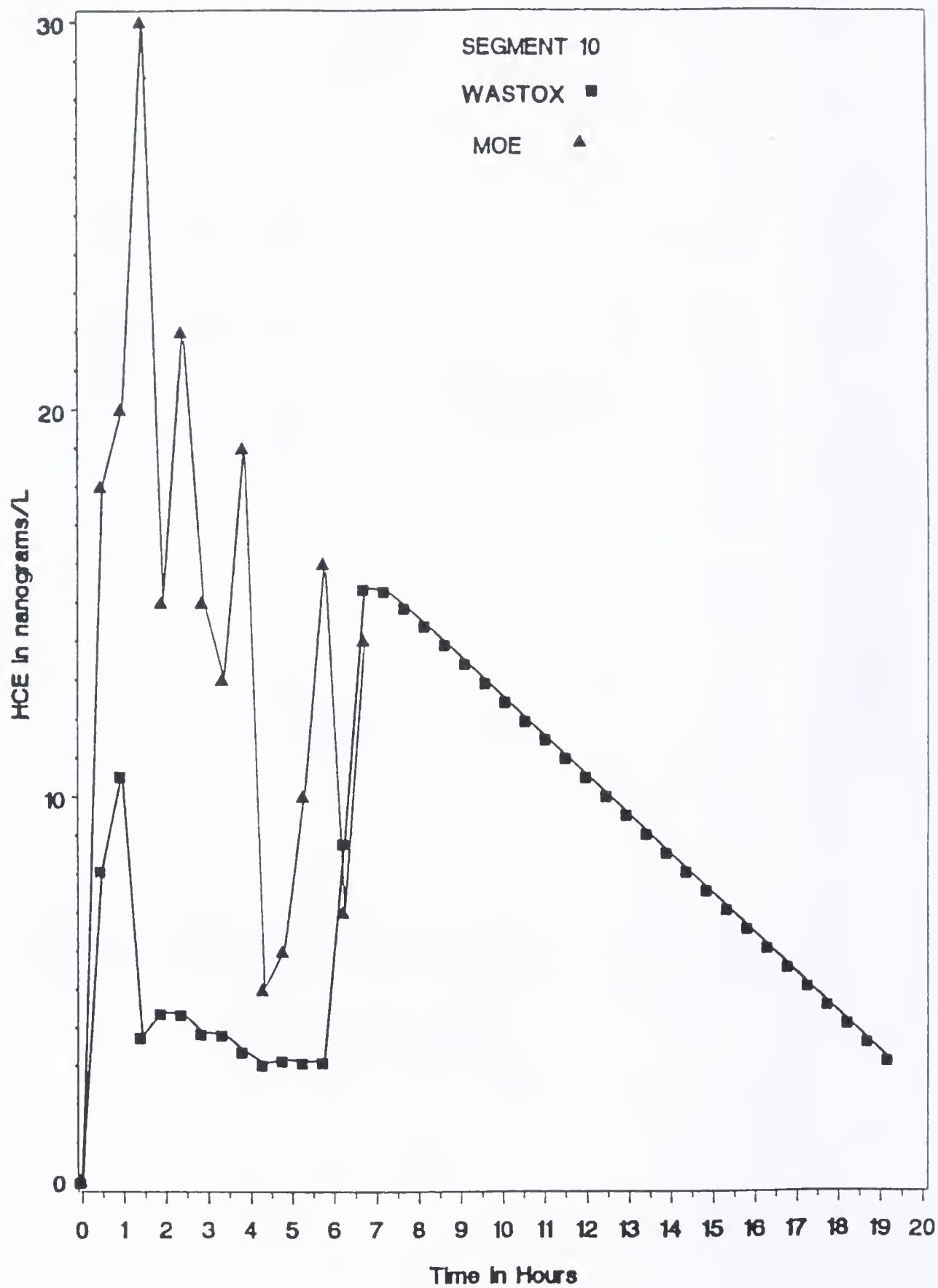


FIGURE 4.1.40: St. Clair River - WASTOX - Fine Grid HCE  
Concentration In Spring



and 90 percentile bounds are also indicated. The HCE and HCB includes the load from the Cole drain. The measured ambient concentrations exceeded the predicted by about 20%. This was considered to be reasonable for calibration in light of the possible buoyant plume effects during the May cruise, as discussed in more detail in the verification section which follows.

The standard deviation in the model output concentrations is generally less than that for the measurements. This is consistent with the fully mixed assumption that is made for each cell in the model.

### (iii) Verification of the WASTOX Model

All of the data from the sequential data set of the July and October cruises plus the unused data from cruise 1 were used for verification. This gave a total of 52, seven hour ambient records and 13 effluent loading records.

The differences between measured and predicted ambient concentrations were assessed using the Students "t" test to determine whether or not the differences could be attributed to the randomness of the ambient data and the load variations alone. The results of this analysis are given in Table 4.1.10 for the calibration Parameters HCE and HCB. A 5% level of significance was used.

A preliminary examination of the data revealed that there was a general decrease in the level of the ambient concentration relative to the outfall concentrations with successive cruises, i.e., for a unit mass loading, the spring ambient concentrations tended to be higher than for the summer and the summer tended to be higher than for the fall. This trend is particularly evident for PERC, Carbon tetrachloride and HCB as shown in Figure 4.1.38. This figure shows the ratio of the measured to the predicted ambient concentrations for PERC and HCB for fine grid cells 5, 10 and 12 for the May, July and October cruises. The measurements were about 50% higher than the

TABLE 4.1.10: STATISTICAL COMPARISON OF CONCENTRATIONS IN SAMPLED CELL

## CASE I - HCE

Cell Number	MEASURED		WASTOX PREDICTED		"t" test	Remarks
	MEAN	STD.DEV.	MEAN	STD.DEV.		
#5	42.13	43.66	13.00	11.18	3.40	NG
#10	14.00	7.60	8.30	3.85	2.90	NG
#12	8.47	7.44	7.75	2.58	.37	OK
#18	4.93	5.26	5.18	1.03	-.20	OK

## CASE II - HCB

#5	16.90	44.32	9.80	14.26	.33	OK
#10	3.00	2.83	3.82	4.81	-1.06	OK
#12	17.30	56.17	32.00	3.20	.97	OK
#18	.20	.56	.74	.41	-3.53	NG

NG = 95% chance that randomness does not account for model observed differences.



model for the July data and more than 100% higher than the model for the May data. This trend is not as clear for the HCB and HCE data sets as indicated by Figure 4.1.37, nevertheless, the May and July measurements tend to be higher than the October measurements in relation to the respective loads. Excluding the HCE October data set, there is fairly good agreement between the model results and the measurements for the HCB and HCE data. The reader is referred to McCorquodale and Yuen (1987) for additional details on the model calibration and verification.

In comparing the measured and ambient results it must be kept in mind that the model averages over a cell volume that is at least 300m long and 10 to 100m wide; in this way the model smooths out the sharp peaks in the outfall concentrations. The model does not explicitly include buoyancy effects. Similarly, the effects of secondary current, due for example to wind, cannot be fully represented in the model.

The trend in the relative concentration, as shown in Figure 4.1.38 and to a lesser extent in Figure 4.1.37, could result from various physical phenomena. The plumes from one or more of the major outfalls may have been more buoyant in the spring, then more completely mixed, as the ambient water temperature increased during the summer. The model concentrations all represent depth and cell averages. While in a buoyant (surface) plume, the measurements taken at 1 m below the water surface would probably be within the high concentration portion of the plume. Abdel-Gawad (1985) found, using a large scale model of a Great Lakes Connecting Channel, that a strong buoyant plume could persist for a considerable distance beyond the normal near field mixing zone and result in surface concentrations about double the depth averaged values. Field observations conveyed to MOE personnel by divers indicate that there was a buoyant plume at the Cole drain outfall in the spring of 1986.

Another possible explanation for the apparent decreasing trend in the ambient data relative to the outfall concentrations (via predicted ambient concentrations) is that the free-phase volatiles may have been concentrated at or near the bottom of the invert of the outfall and

thus were not represented in the sample. This material would not be reflected in sewer sampling since this occurred at mid-depth in the pipes. For a buoyant plume, some of this may be mixed and lifted or dissolved to appear in the near surface ambient samples. For a well mixed or sinking plume, the chemical at the bottom of the outfall would tend to give higher concentrations in the lower part of the receiving water column. Denser than water chemicals such as PERC (with a high specific gravity) may appear as droplets and settle out on the river bed. Surface samples would then underestimate the depth averaged concentration that is represented by the model output. This phenomenon is consistent with the observed trends in Figures 4.1.37 and 4.1.38. The above effects could potentially apply to non-volatiles like HCB and HCB that are readily dissolved in liquid PERC or CCL<sub>4</sub> or are strongly partitioned to suspended solids. The settling-out of the suspended solids would lower the surface concentrations of these contaminants. These effects would not become important for the nearfield 10 to 30m downstream of the outfall since settling velocities of the suspended solids is small and turbulent mixing is large. It is also possible that in-place pollutants contributed to higher ambient concentrations of contaminants in May and July as compared to October.

The WASTOX model was used to investigate the possibility of an in-place source of contaminants that was gradually depleted from May to October. Although it was shown that this could account for discrepancies at cells 12 and 18, it did not account for the trend at cell 5. This may be due to the fact that contaminated material does not reach the riverbed for a significant distance ( $\approx 30\text{m}$ ) downstream of the outfall.

Some other reasons for disagreement between the model and the measurements are: (a) the model assumes uniform and complete mixing in the receiving water cell, while in practice this cell has high concentration gradients due to the near field mixing; (b) the measured samples cannot fully represent the variability of concentrations in this cell nor can they represent the average conditions that the model

assumes; (c) the half hour sampling of the outfall and the receiving waters were out of phase, which could lead to large relative errors for very flashy changes in input concentrations; (d) the half hour sampling may have missed some peaks in the outfall loads; these peaks may show up in the samples of the receiving waters because of the temporal and spatial spreading due to initial turbulent mixing; (e) some of the measurements were near the method detection levels especially at cell 18; (f) numerical instability and numerical dispersion may have contributed to some of the error (however, this is expected to be a minor problem since the model step time was selected to avoid instability and the dispersion coefficients were adjusted in the calibration procedures to give the observed mean concentration gradients).

Table 4.1.11 Case (a) represents the measured to predicted concentration ratios for all stations and all three cruises.

Table 4.1.11 Case (b) the measured data have been corrected for the effect of the buoyant plume. Table 4.1.11 Case (c) shows the ratios when the following corrections are applied:

- (i) the spring and summer raw data corrected to the depth averaged conditions based on a buoyant plume (using Abdel-Gawad (1985); the spring ambient data were corrected by a factor of 0.6 for cells 5, 10 and 12 and a factor of 0.8 for the summer);

Some contaminants (PERC and CCL<sub>4</sub>) may be partly in immiscible form and settle out of the plume. Other chemicals (HCB<sub>D</sub>, HCB, HCE) are sorbed to the suspended solids in the effluent; some of these will tend to settle out before the chemicals are desorbed to the water in the plume. Based on the typical silt settling velocities and river velocities, the suspended solids will reach the bed at between 30 and 1000m downstream of the outfall. At the same time desorption will occur and re-entrainment of previously contaminated solids will increase the contaminant concentration in the water column. These errors are difficult to estimate and therefore are grouped with correction (ii) for mean loadings.

(ii) a correction of 1.5 was applied to the predicted ambient volatiles to correct for possible underestimation of the actual load while a factor of 1.2 was applied to HCB and HCE for May and July.

In summary, the calibration runs for HCB and HCE calculated an average ratio (uncorrected) of 1.2 (measured to predicted). The verification runs for HCB and HCE calculated an uncorrected ratio of 1.05 with a range from 0.3 to 3.0. The average uncorrected ratio for PERC, HCB and CCL4 is 1.6 with a range from 0 to 4. When all the corrections are applied to all the stations, the overall ratio of measured to predicted is 0.97 with a range of 0 to 2.5.

(e) Concluding Remarks

Table 4.1.11 shows the WASTOX model can represent the mean response of the St. Clair River to contaminant loadings which have periods of fluctuation greater than one-half hour. In order to properly represent the near field concentrations, it is necessary to account for buoyancy, settling and sorption effects.

4.1.4 Effluent Toxicity

(a) Introduction

Toxicity testing of whole effluent wastewater discharges with the rainbow trout 96-hour static acute lethality test has been the cornerstone of MOE biological assessment since the early 1970's. The application of effluent acute toxicity requirements is based on existing Ministry surface water quality policy, published in "Water Management-Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment", known as the "Blue Book" (MOE 1984).

Effluent toxicity testing is referred to directly in Policy #3-Effluent Requirements. Here it is stated that 96-hour bioassays

TABLE 4.1.11(a): RATIO OF MEASURED TO PREDICTED CONCENTRATIONS FOR ALL RUNS

CASE	CELL	HCB	HCE	SPRING			HCB	HCE	SUMMER			HCB	HCE	FALL		
				HCBD	PERC	CCL4			HCBD	PERC	CCL4			HCBD	PERC	CCL4
(a)																
RAW	OUTFALL	1.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
DATA	No. 5	1.4*	1.7*	2.20	3.00	2.20	2.00	1.00	1.50	1.70	1.70	1.00	.30	.40	.85	.80
	No. 10	1.4*	1.35*	2.20	2.80	3.00	1.30	1.40	2.00	.18	.80	.90	.50	.60	.90	1.00
	No. 12	1.35*	1.0	1.70	1.40	3.00	3.00	.90	2.10	4.00	2.20	1.10	.40	1.00	1.00	1.30
	No. 18	0.5*	0.8*	3.00	3.00	3.00	.90	1.00	3.00	3.00	.00	.80	.30	1.60	.00	.00
* Calibration points																

TABLE 4.1.11(b): RATIO OF MEASURED TO PREDICTED CONCENTRATIONS FOR ALL RUNS

CASE	CELL	HCB	HCE	SPRING			HCB	HCE	SUMMER			HCB	HCE	FALL		
				HCBD	PERC	CCL4			HCBD	PERC	CCL4			HCBD	PERC	CCL4
(b)																
PLUME	OUTFALL	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
EFFECT	No. 5	.90	1.00	1.30	1.80	1.30	1.60	.80	1.20	1.40	1.40	1.00	.30	.40	.85	.80
	No. 10	.85	.80	1.30	1.70	1.80	1.00	1.10	1.60	1.40	.60	.90	.50	.60	.90	1.00
	No. 12	.80	.60	1.00	.85	1.80	2.40	.80	1.70	3.00	1.80	1.10	.40	1.00	1.00	1.30
	No. 18	.50	.80	3.00	3.00	3.00	.90	1.00	3.00	3.00	.00	.80	.30	1.60	.00	.00

TABLE 4.1.11(c): RATIO OF MEASURED TO PREDICTED CONCENTRATIONS FOR ALL RUNS

CASE	CELL	HCB	HCE	SPRING			HCB	HCE	SUMMER			HCB	HCE	FALL		
				HCBD	PERC	CCL4			HCBD	PERC	CCL4			HCBD	PERC	CCL4
(c)																
PLUME	OUTFALL	1.00	.83	.83	.67	.67	1.00	.83	.83	.67	.67	1.00	1.00	1.00	1.00	1.00
S.G.	No. 5	.90	.70	1.00	1.10	1.20	1.60	.70	1.00	.90	.90	1.00	.30	.40	.85	.80
	No. 10	.85	.70	1.00	1.10	1.20	1.00	.90	1.30	.90	.40	.90	.50	.60	.90	1.00
	No. 12	.80	.55	.85	.60	1.20	2.40	.70	1.40	2.00	1.20	1.10	.40	1.00	1.00	1.30
	No. 18	.50	.70	2.50	2.00	2.00	.90	.90	2.50	2.00	.00	.80	.30	1.60	.00	.00



may be required to identify discharges that are deleterious to aquatic life. Undiluted effluents which induce a toxic reaction as measured by the 96-hour static bioassay, may lead to the need for additional treatment of wastewater to afford adequate protection to the aquatic environment.

(b) Methods

Samples of Dow effluent were obtained from the 1st Street 42-inch sewer on June 11, 1986 and from the 4th Street Sewer on May 30 1986 and tested at the MOE laboratories in Rexdale. The methods used to obtain and test the effluent are given in Craig et al. (1983).

(c) Results

As summarized in Table 4.1.12, the tested effluents were found not to be acutely lethal to rainbow trout in the 96 hr. exposure period.

The Mixing Zone Policy (Policy 5) of the "Blue Book" states that rapid lethality to important aquatic life is not permitted within a mixing zone. This includes the area in close proximity to the discharge prior to significant mixing. As such, end-of-pipe testing has become the most appropriate control point for measurement of acute lethality to fish. Since Dow effluents were non-lethal, they did not violate Policy 5.

TABLE 4.1.12: RESULTS OF 96 HR. STATIC ACUTE LETHALITY TEST ON WHOLE EFFLUENTS OF DOW

COMPANY	EFFLUENT	SAMPLE DATE	% EFFLUENT (LETHALITY)
DOW	1st St. 42-inch Sewer	06/11/86	100% (non lethal)
		06/11/86	100% (non lethal)
		06/11/86	100% (non lethal)
	4th St. Sewer	09/18/86	100% (non lethal)

## 4.2 Ambient Water Quality Monitoring

### 4.2.1 Centrifugation

#### (a) Introduction

To better understand the behaviour, fate and transport of a chemical discharged from an industrial source, it is useful to document its partitioning characteristics. This provides insight into a compounds affinity for the dissolved or aqueous phase and the particulate phase in the receiving water.

Through centrifugation of a large volume of water/effluent, the associated suspended fraction can be isolated from the aqueous fraction. This provides several important benefits:

- (i) An estimate of a compounds partitioning and the extent to which an equilibrium condition between the aqueous and solid phases, through comparisons with literature values.
- (ii) Quantification of compounds not easily detected in whole water/effluent grab samples (1 litre), due to the concentration of fine solid material from a large volume of water/effluent (2000-3000 litres).
- (iii) The ability to estimate whole water/effluent concentrations given the concentration measured on suspended solids, the amount of suspended material, and a specific chemicals partitioning coefficient ( $K_{ow}$ ). Several modifying factors such as the organic carbon content of the solid fraction and the state of equilibrium are important here.

#### (b) Methods

Two centrifuging components were undertaken to document contaminants associated with suspended solids. One component, which was briefly



discussed (see Section 4.1.2), focussed on centrifuging industrial outfalls from Dow Chemical and Polysar. The second involved sampling St. Clair River water from the surface and bottom and occasionally at mid-depth. The ambient sampling locations are outlined in Figure 4.2.1 and Table 4.2.1.

Water was pumped from the depths indicated by means of a March 5C-MD submersible pump and carried through a teflon hose. All pump, hose and fittings in contact with sample water were teflon or stainless steel.

Quarterly composite grab samples were obtained during the initial cruise (May 1988) from the influent prior to centrifugation and from the effluent side of the centrifuge. These latter samples had the solids removed as a function of the efficiency of the centrifuge. Approximately 25 gm wet weight of solid "fines" were collected for analysis. During subsequent cruises, only composite influent and centrifuged material was collected for analysis.

Samples were analysed for an extensive list of parameters as outlined in Table 4.1.1 (effluent/water) and Table 4.2.2 (solids) as well as heavy metals lead, cadmium, mercury and nutrients. Where sufficient sample size was available, particle size analysis was conducted on solids.

## (c) Results and Discussion

### (i) Centrifuging in the St. Clair River and at Industrial Outfalls

#### Proportion of Contaminants in Aqueous vs. Solid Phases

Organic chemicals partition according to several factors. These may include a chemicals hydrophobicity/lipophilicity, its affinity for material in suspension, the organic carbon content of the solids as well as a number of other factors (Gobas and Mackay 1989).

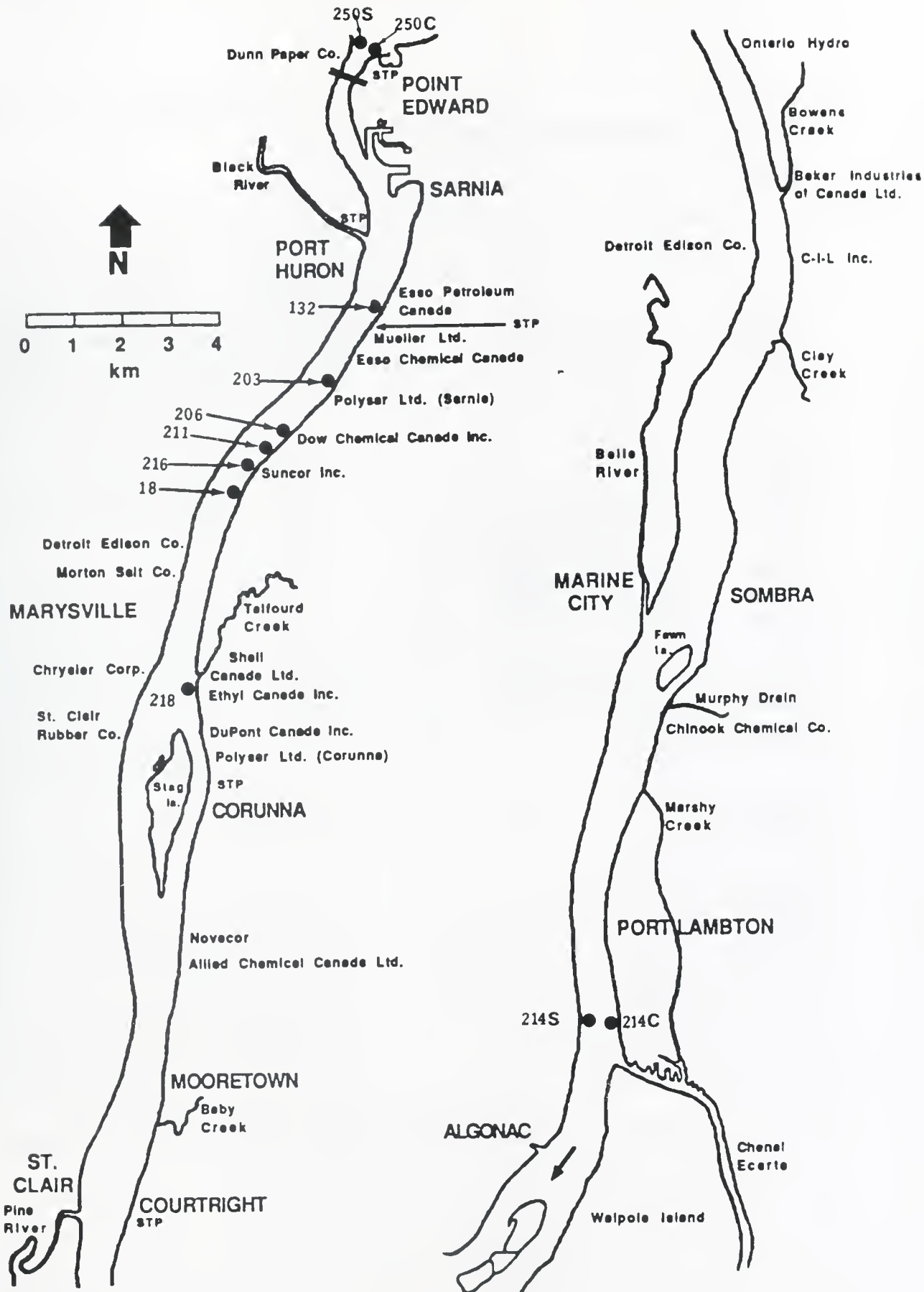


FIGURE 4.2.1: ST. CLAIR RIVER AMBIENT CENTRIFUGING STATIONS

TABLE 4.2.1: CENTRIFUGING SAMPLING LOCATIONS

STATION NUMBER	LOCATION	DIST. FROM CANADIAN SHORE (m)	SURF.	MID.	BOTTOM
<u>AMBIENT</u>					
25C	SR 39.0	100		X	
25US	SR 39.0	366		X	
132	d/s CN Tunnel	30	X		X
203	d/s Cole drain diffuser	68	X		X
206	d/s 1st St. Sewers	10	X		X
211	d/s 3rd St. Sewers	10	X		X
216	SR 33.8	30	X		X
18	SR 33.4	30	X		X
218	d/s Talfourd Creek	100	X		X
214C	SR 12.9	120		X	
214US	SR 12.9	550		X	
<u>EFFLUENT</u>					
15 07	Cole drain	0		X	
03 620	Polysar Biox	0		X	
03 220	Polysar 72"	0		X	
91 220	Dow 42"	0		X	
91 320	Dow 48"	0		X	
91 520	Dow 54" Sluice	0		X	
91 720	Dow 3rd St.	0		X	
91 920	Dow 4th St.	0		X	

d/s - downstream

TABLE 4.2.2: CENTRIFUGED SOLIDS PARAMETER LIST

<u>Volatile Organic Compounds:</u>	<u>Chlorinated Aromatic Compounds:</u>
Dichloromethane	Hexachloroethane
1,1-Dichloroethylene	1,3,5-Trichlorobenzene
Bromochloromethane	1,2,4 Trichlorobenzene
1,1-Dichloroethane	Hexachlorobutadiene
Chloroform	1,2,3-Trichlorobenzene
1,2,-Dichloroethane	2,4,5-Trichlorotoluene
1,1,1-Trichloroethane	2,3,6-Trichlorotoluene
Carbon tetrachloride	1,2,3,5 Tetrachlorobenzene
Dichlorobromomethane	1,2,4,5 Tetrachlorobenzene
1,2-Dichloropropane	2,6,a-Trichlorotoluene
Benzene	1,2,3,4-Tetrachlorobenzene
Trichloroethylene	Pentachlorobenzene
1,1,2-Trichloroethane	Hexachlorobenzene
Chlorodibromomethane	Octachlorostyrene
1,2-Dibromoethane	
Bromoform	Detection limit: 1 ng/g (1 ppb)
1,3-dichlorobutane	
Tetrachloroethylene	
Toluene	
1,1,2,2-Tetrachloroethane	
Chlorobenzene	
Ethylbenzene	
m-Xylene	
o- or p-Xylene	
1,2-Dichlorobenzene	
Detection limit: 10 ng per sample (dependent upon sample size)	

Additional factors, such as a chemicals equilibrium state with respect to partitioning on a site specific basis, may be important. Oliver (1987) indicated that the proximity of sampling to a point source may affect the proportion of contaminants in the solid or aqueous phase. Time to achieve equilibrium may be such that it is not attained until a compound has been exposed to the receiving water for 12-24 hours.

The St. Clair River Spill Manual (Nettleton and Hamdy 1988), developed to provide early warning of the effects of chemical spills on downstream water intakes, suggests a mean travel time of 13 hours for a spill to travel from the "Chemical Valley" (i.e., Dow vicinity) to the Lake St. Clair delta. Based on this information, a true estimate of equilibrium partitioning would not be possible until Lake St. Clair.

Table 4.2.3 provides a sample of contaminant levels associated with suspended solids normalized to a 1 l volume. This permits a comparison of contaminants associated with solid and aqueous phases, by subtracting calculated levels on solids from measured levels in whole water (Figures 4.2.2 - 4.2.4). It is particularly evident that compounds such as HCB and OCS are almost exclusively associated with suspended solids, while tetrachloroethylene is primarily dissolved. This is to be expected, since the first two compounds are extremely hydrophobic, with relatively high log  $K_{ow}$  values in the 3.7 to 6.5 range. The solubility of HCB approaches 2 ppm and is therefore at an intermediate level while tetrachloroethylene is soluble to 150 ppm. This may explain the tendency to equilibrate towards the aqueous fraction (Table 4.2.3 Figure 4.2.3).

TABLE 4.2.3: PARTITIONING OF CONTAMINANTS BETWEEN AQUEOUS AND SOLID PHASES

COMPOUND	LOCATION	MEASURED LEVELS OF			CONTAMINANT DISTRIBUTION WITHIN 1 LITRE OF EFFLUENT			
		CONT. ON SOLIDS <sup>1</sup> ng/g	CONT. IN WHOLE EFFLUENT ng/L	SUSP. SOLIDS <sup>3</sup> mg/L	ON SOLIDS <sup>4</sup>		NOT ON SOLIDS <sup>5</sup>	
					ng/L	(%)	ng/L	(%)
HCB	Dow 42" Sewer	67,986	124	4.3	292.3	(100%)	0	(0%)
	206	90	4	18.1	1.63	( 41%)	2.37	(59%)
	214C	168	1	10.1	1.70	(100%)	0	(0%)
PERC	Dow 42" Sewer	2,800	44x10 <sup>3</sup>	5.8	16.2	(0.04%)	43.98x10 <sup>3</sup>	(99.96%)
	206	65	4x10 <sup>3</sup>	3.2	0.208	(0.01%)	3.99x10 <sup>3</sup>	(99.99%)
	18	255	6x10 <sup>3</sup>	5.3	1.35	(0.02%)	5.99x10 <sup>3</sup>	(99.98%)
OCS	Dow 42" Sewer	47,900	147	4.1	196.4	(100%)	0	(0%)
	18*	353	4	3.0	1.06	(26.5%)	2.94	(73.5%)
HCBd	Dow 42" Sewer	13,000	9	5.8	75.4	(100%)	0	(0%)
	18*	255	4.5	2.2	0.56	(12.4%)	3.94	(87.6%)

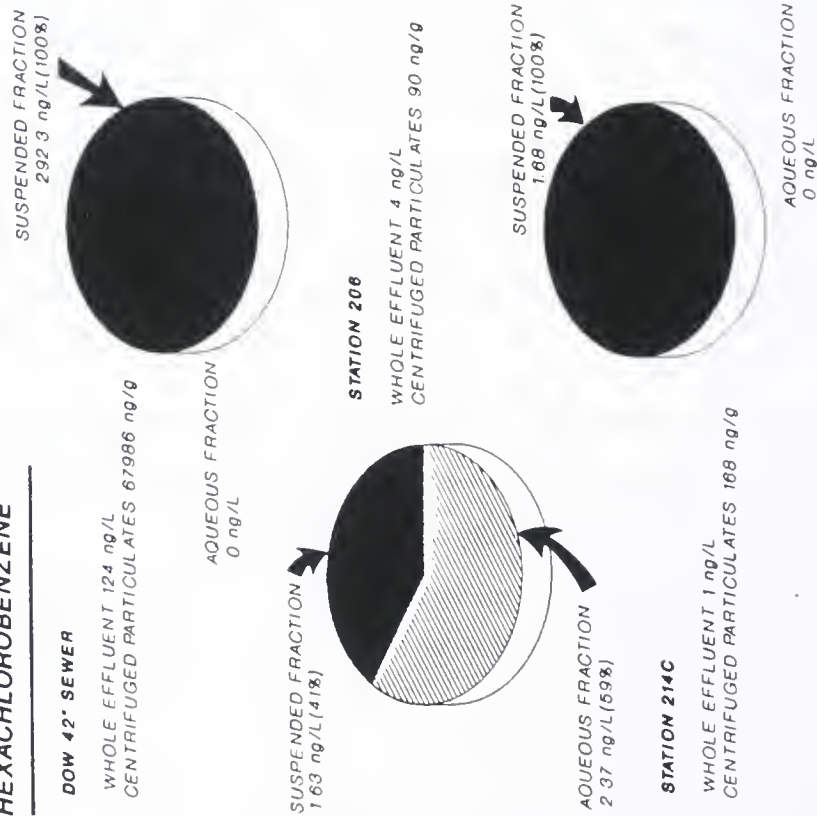
LEGEND:

- <sup>1</sup> - Concentration obtained through direct measurement of solids removed from whole water
- <sup>2</sup> - Concentration obtained through direct measurement of sample of whole water
- <sup>3</sup> - Concentration of suspended material in 1 l of whole water
- <sup>4</sup> - Concentration of contaminant on solids expressed on a 1 l volume basis
- <sup>5</sup> - Amount of contaminant not accounted for by solids (i.e. in aqueous phase)
- \* mean of surface and bottom samples



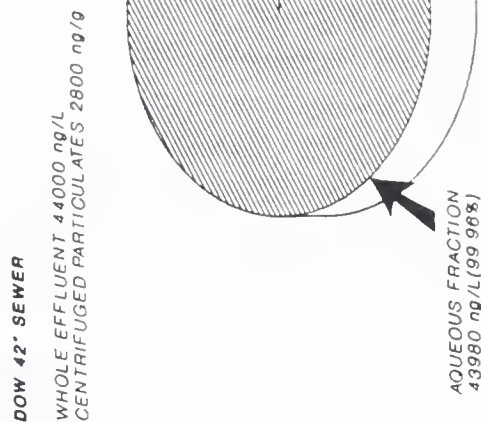
**FIGURE 4.2.2: WHOLE EFFLUENT/WATER  
CONTAMINANT LOAD ACCOUNTED FOR BY  
SUSPENDED/AQUEOUS FRACTIONS**

**HEXACHLOROBENZENE**



**FIGURE 4.2.3: WHOLE EFFLUENT /WATER  
CONTAMINANT LOAD ACCOUNTED FOR BY  
SUSPENDED/AQUEOUS FRACTIONS**

**TETRACHLOROETHYLENE**





**FIGURE 4.2.4 : WHOLE EFFLUENT/WATER  
CONTAMINANT LOAD ACCOUNTED FOR BY  
SUSPENDED/AQUEOUS FRACTIONS**

**HEXACHLOROBUTADIENE**

SUSPENDED FRACTION  
75.4 ng/L (100%)



**DOW 42° SEWER**

WHOLE EFFLUENT 9 ng/L

CENTRIFUGED PARTICULATES 13000 ng/g

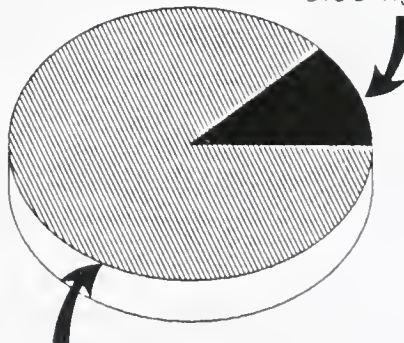
AQUEOUS FRACTION  
0 ng/L

**STATION 18**

WHOLE EFFLUENT 4.5 ng/L

CENTRIFUGED PARTICULATES 255 ng/g

SUSPENDED FRACTION  
0.56 ng/L (12.4%)



AQUEOUS FRACTION  
3.94 ng/L (87.6%)

### Centrifuging Efficiency

A brief comparison of the solids removal efficiency of the Westfalia centrifuge indicates the following:

STATION	DATE	SUSPENDED SOLIDS (mg/L)		% FINE MATERIAL (<3.7 $\mu$ m)	% REMOVAL
		Pre	Post		
25US MID.	86/05/16	1.8	0.1	83.4	94.5
25C MID.	86/05/15	1.9	0.5	51.3	73.7
206 BOTT.	86/05/11	3.9	0.7	29.6	82.1
211 SURF.	86/05/10	5.6	1.7	44.9	69.7
211 BOTT.	86/05/10	5.1	1.0	41.8	80.4
216 SURF.	86/05/09	4.6	0.6	22.7	87.0
216 BOTT.	86/05/09	4.7	0.7	22.7	85.2
18 SURF.	86/05/07	2.4	0.6	30.5	75.0
18 BOTT.	86/05/07	2.0	0.4	14.7	80.0
218 SURF.	86/05/08	3.6	0.8	60.5	77.8
218 BOTT.	86/05/08	4.4	0.6	95.2	86.4
214C MID.	86/05/19	8.5	0.6	96.4	93.0
214US MID.	86/05/19	6.5	0.6	39.5	90.8

Solids removal efficiency was typically 80% and above. The highest removal occurred at the head and mouth stations 25 and 214 respectively along the Canadian shore, where 94.5 and 93% of the solids were removed.

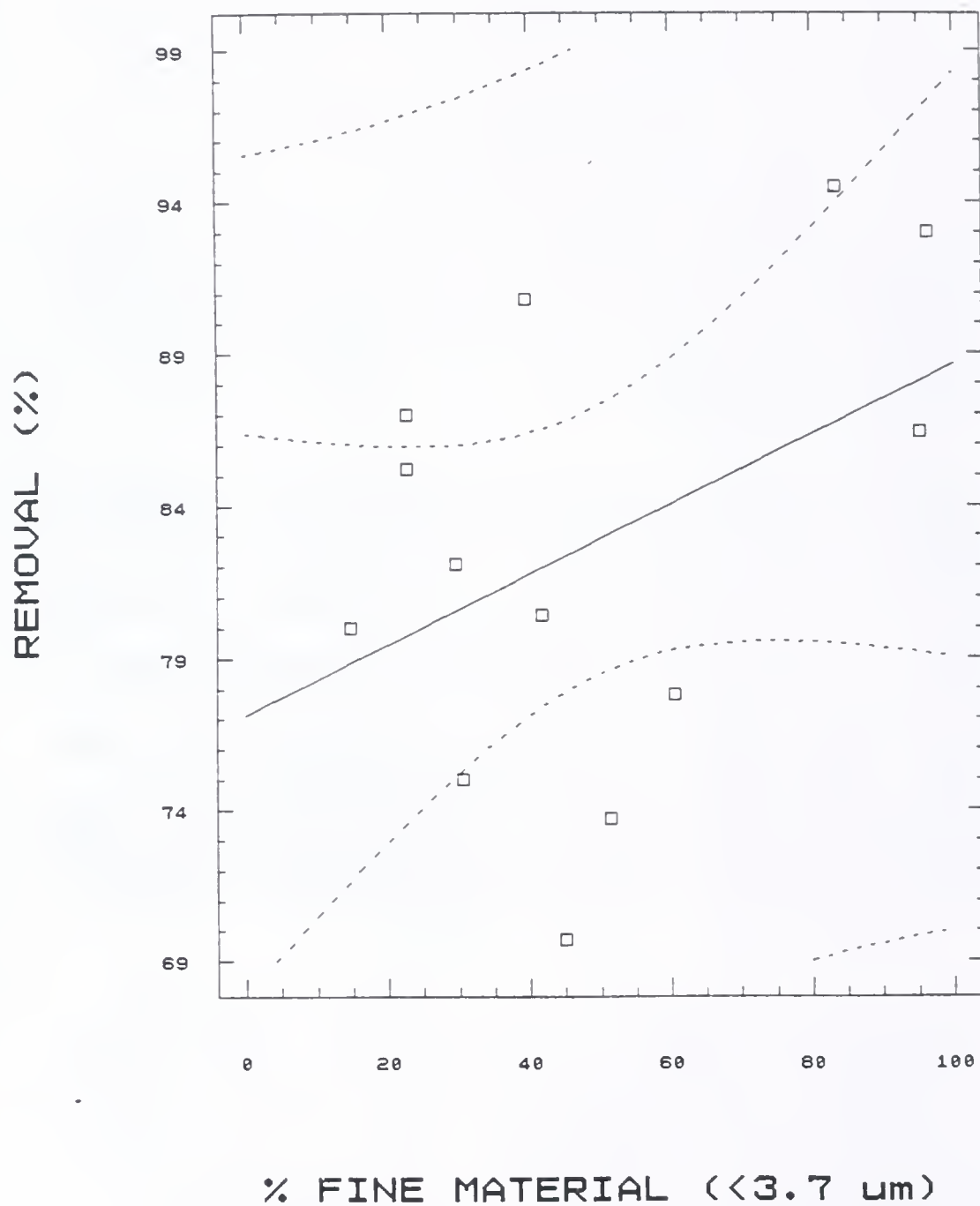
There appears to be a somewhat tenuous correlation between removal efficiency and particle size. In most instances, improved removal is achieved if there is a greater proportion of fine material. Figure 4.2.5(a) demonstrates this relationship for varying depths at centrifuging stations. Figure 4.2.5(b) presents size distribution of solids removed through centrifugation. A general increase is observed in removal with decreasing particle size. However, the relationship is not statistically significant, as the correlation coefficient is 0.42 with an R-squared equal to 17.3%. The relationship becomes significant at an  $\alpha$  level of 0.16.

It should be noted that in some cases, suspended solid contaminant concentrations normalized to one liter of water, overpredict actual measurements in whole water samples. This may be due, in part, to obtaining a whole water sample not representative of the centrifuged material. It was hoped that the problem would be avoided through obtaining quarterly grab samples in the field, and producing a composite sample in the lab. Problems may have arisen in this regard if losses to the bottled headspace occurred during storage; and subsequently lost to the atmosphere. Selection of an alternate sample container, such as a cap with a teflon septum, allowing a syringe to obtain an aliquot may be more appropriate.

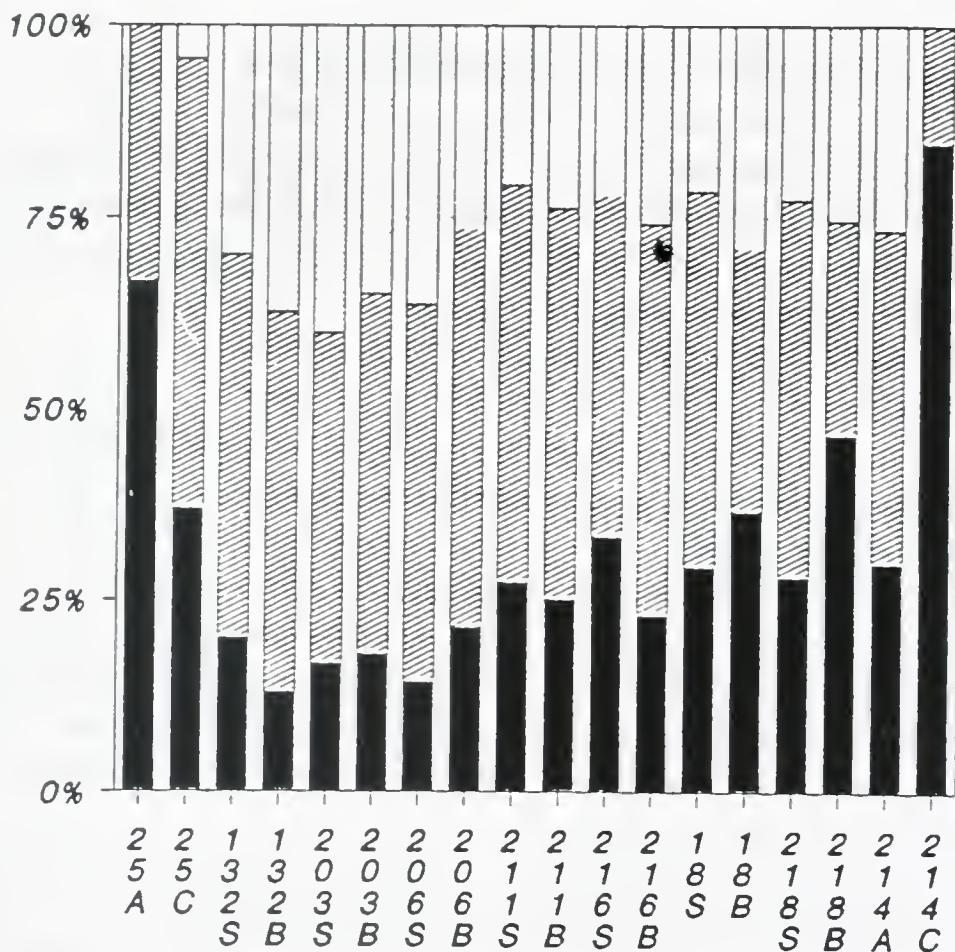
A further possibility may account for inaccuracies in whole water concentrations, particularly in the receiving water. Ambient levels often approach the laboratory Method Detection Limit (MDL), typically 1 ng/L for chlorinated aromatic compounds such as HCB, HCBD and OCS. Laboratory protocols for reporting this information generally state that values less than 10X the MDL are tentative and may be semi-quantitative. These concentrations are observed for both HCB and HCBD at station 214C and the Dow 42-inch sewer respectively (Table 4.2.3).

FIGURE 4.2.5a

# REMOVAL EFFICIENCY vs. % FINES



**FIGURE 4.2.5b : SIZE FRACTIONATION  
FOR CENTRIFUGED SOLIDS**



CLAY
  FINE SILT
  COARSE SILT

A - ADJACENT TO MICHIGAN SHORELINE

C - ADJACENT TO ONTARIO SHORELINE

S - 1m BELOW SURFACE

B - WITHIN 0.2m OF BOTTOM

## Detection of Compounds on Solids Not Observed/Detected in Whole Effluent/Water Samples

While state-of-the-art analytical methods were employed in the analysis of water/effluent samples, many results particularly in the receiving water were below MDL's.

An advantage of removing fine particulate material from 2000-3000 litres of water over a 6-8 hour period results from the concentration of associated contaminants into an analytical range more easily quantified. This is similar in concept to obtaining large volume water samples and subjecting them to solvent extraction, thereby lowering detection levels in proportion to the volume collected (Aqueous Phase Liquid Extraction - APLE).

While both methods are labour intensive and time consuming, they enable the detection of compounds normally undetected in whole water small volume grab samples. In addition to compounds listed in Tables 4.1.1 & 4.2.2 which were analysed for water/effluent and sediment samples by dual capillary column gas chromatography (chlorinated aromatics) or purge-and-trap gas chromatographic analysis with simultaneous flame ionization and electron capture detection (volatile organics - water/effluent only) many additional parameters were detected in suspended solids.

Using a purge-and-trap technique followed by capillary Gas Chromatography/Mass Spectrometry, many additional compounds associated with suspended solids were detected. It should be noted that the method for the determination of volatile organic compounds in sediment is under development and levels should be considered estimates of minimum values.

Currently there are several significant assumptions which may effect quantitative determination in sediments. These assumptions are as follows:



1. The purging efficiency of the compound is identical to that of the internal standard added to each sample.
2. The GC (gas chromatograph) behaviour of the compound is identical to that of the internal standard.
3. The MS (mass spectrometer) response of the compound is identical to that of the internal standard.

Appendices 2 and 4.1 provide a summary of volatile and extractable compounds detected on centrifuged solids from outfall and ambient stations respectively.

Several compounds were identified which were either not detected or not analysed for in whole water/effluent or sediment samples by gas chromatography only.

Some of these include biphenyl, diphenyl ether and their derivatives which are produced at Dow Chemical as "DOWTHERM"<sup>TM</sup>, an insulating/cooling agent. Peak ambient levels (840 ng/g - diphenyl ether; 440 ng/g - biphenyl) were noted at station 18. Peak effluent levels (171 ng/g and 64 ng/g respectively) were measured at the Dow 4th St. sewer.

Additional compounds measured included dimethyl sulphide, chlorinated butadienes and several PAH compounds (methyl naphthalene and naphthalene).

## (ii) Distribution of Selected Parameters on Suspended Solids

### Industrial Outfalls:

One way analysis of variance (ANOVA) conducted on industrial outfall concentrations for selected parameters revealed significant differences between outfalls for the following: phosphorus, loss on ignition and



total organic carbon ( $p < 0.05$ ). Marginally significant differences ( $p < 0.06$ ) were noted between outfalls for 1,2,3,4-tetrachlorobenzene and total Kjeldahl nitrogen.

Subsequent multiple range testing (Tukey's Multiple range test) indicated that the Cole drain and the Polysar biological oxidation treatment effluent accounted for the greatest differences for all parameters except 1,2,3,4-tetrachlorobenzene. In this case, the highest levels were observed at the Cole drain, followed by the Dow 42-inch sewer.

Additional parameters were subjected to ANOVA; however, no significant differences were noted between stations. In most instances levels from the Dow 42-inch sewer were highest but not at a 95% confidence level. Extreme variances in data necessitated log transformation prior to ANOVA. Tests for homogeneity of variance, following transformation suggested homogeneity for all compounds except HCB, HCBd and phosphorus. This leads one to assume that a certain degree of randomness is associated with effluent levels, perhaps related to process changes. Appendices 4.2 (ambient) and 4.3 (effluent) provide a summary of results measured by conventional GC analysis for suspended solids. This provides an indication of the degree of variability associated with these results.

Relative contaminant concentrations following log transformation are presented in Figures 4.2.6 to 4.2.11 for compounds associated with outfall suspended solids.

#### Ambient Water Stations:

Ambient centrifuging data was subjected to a two-way ANOVA to determine the differences between stations as well as depths. This latter comparison enabled the degree of vertical mixing and the significance of bottom water transport of resuspended material to be assessed.

FIGURE 4.2.6

# PHOSPHORUS ON SUSP. SOLIDS ANOVA BOXPLOT (95% C.I.)

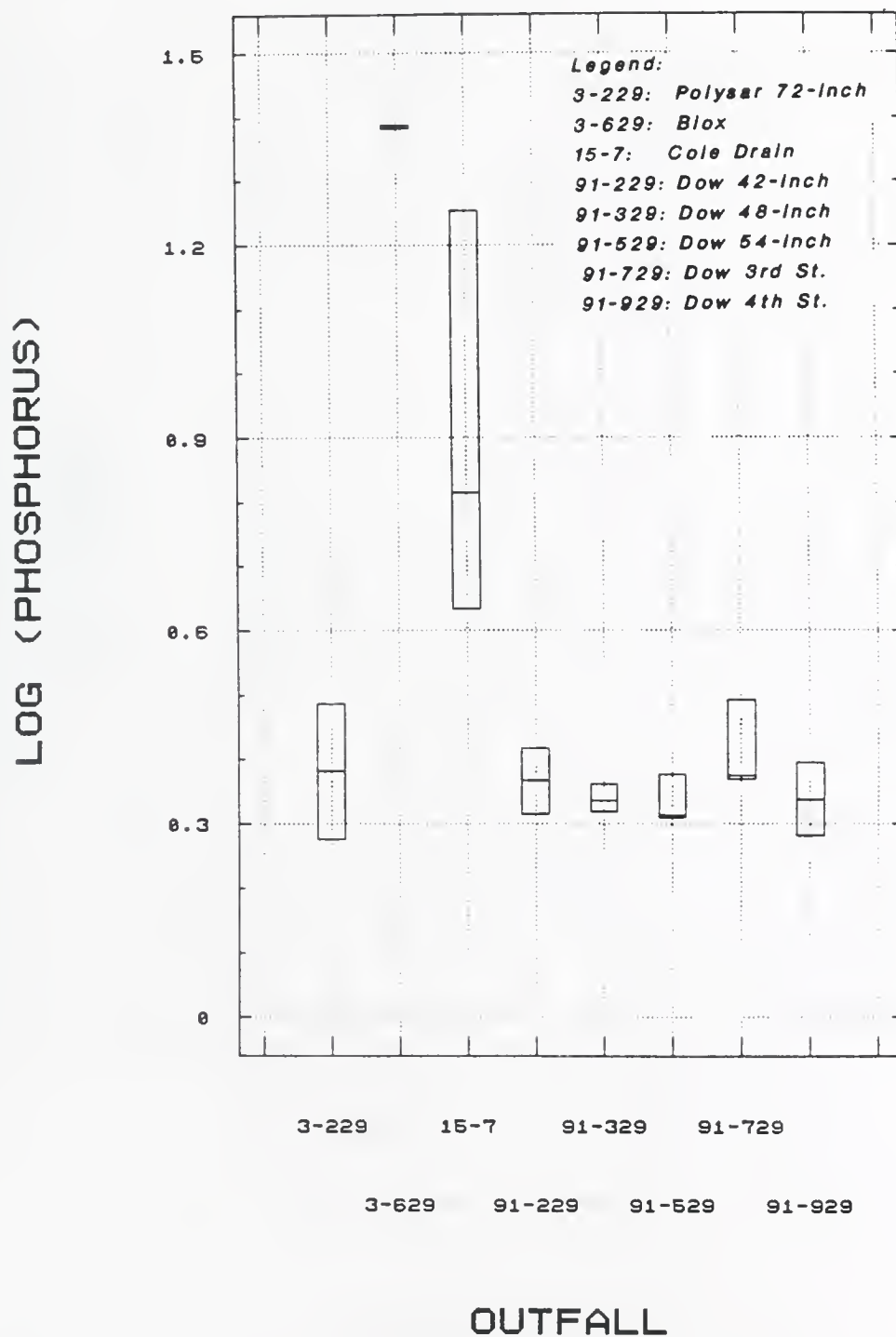


FIGURE 4.2.7

# MERCURY ON SUSP. SOLIDS ANOVA BOXPLOT (95% C.I.)

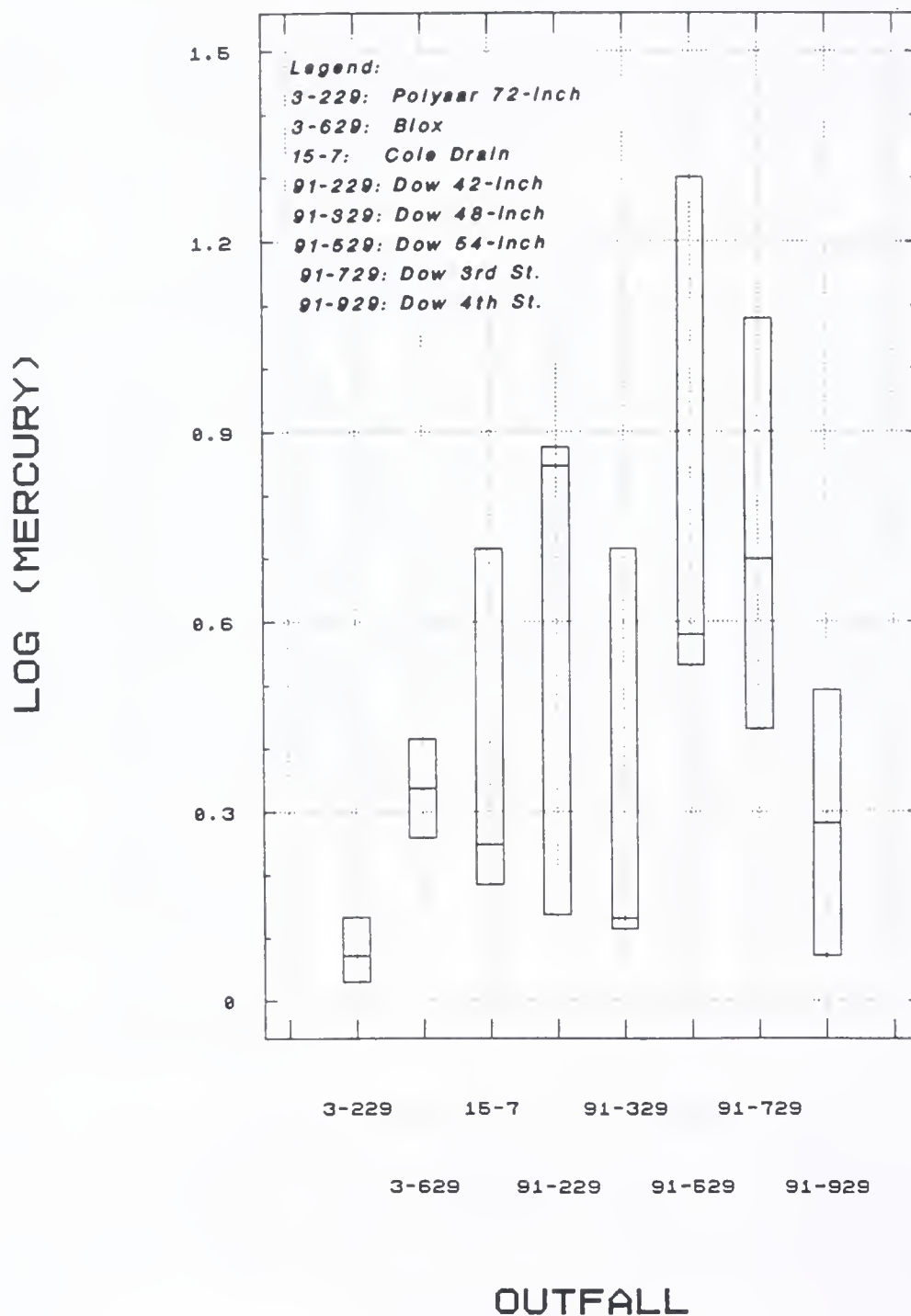


FIGURE 4.2.8

# HCBD ON SUSPENDED SOLIDS ANOVA BOXPLOT (95% C.I.)

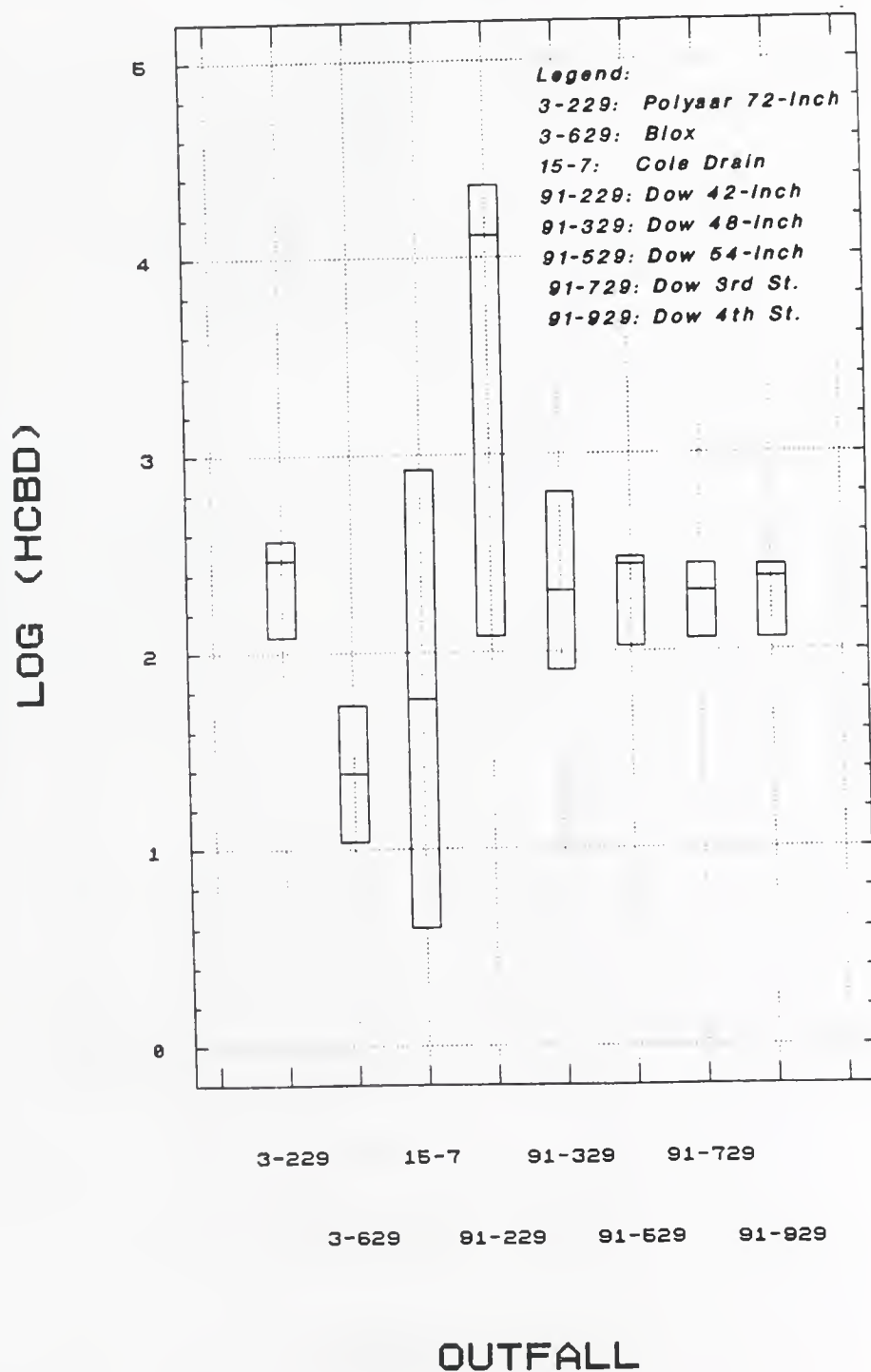


FIGURE 4.2.9

# HCB ON SUSPENDED SOLIDS ANOVA BOXPLOT (95% C.I.)

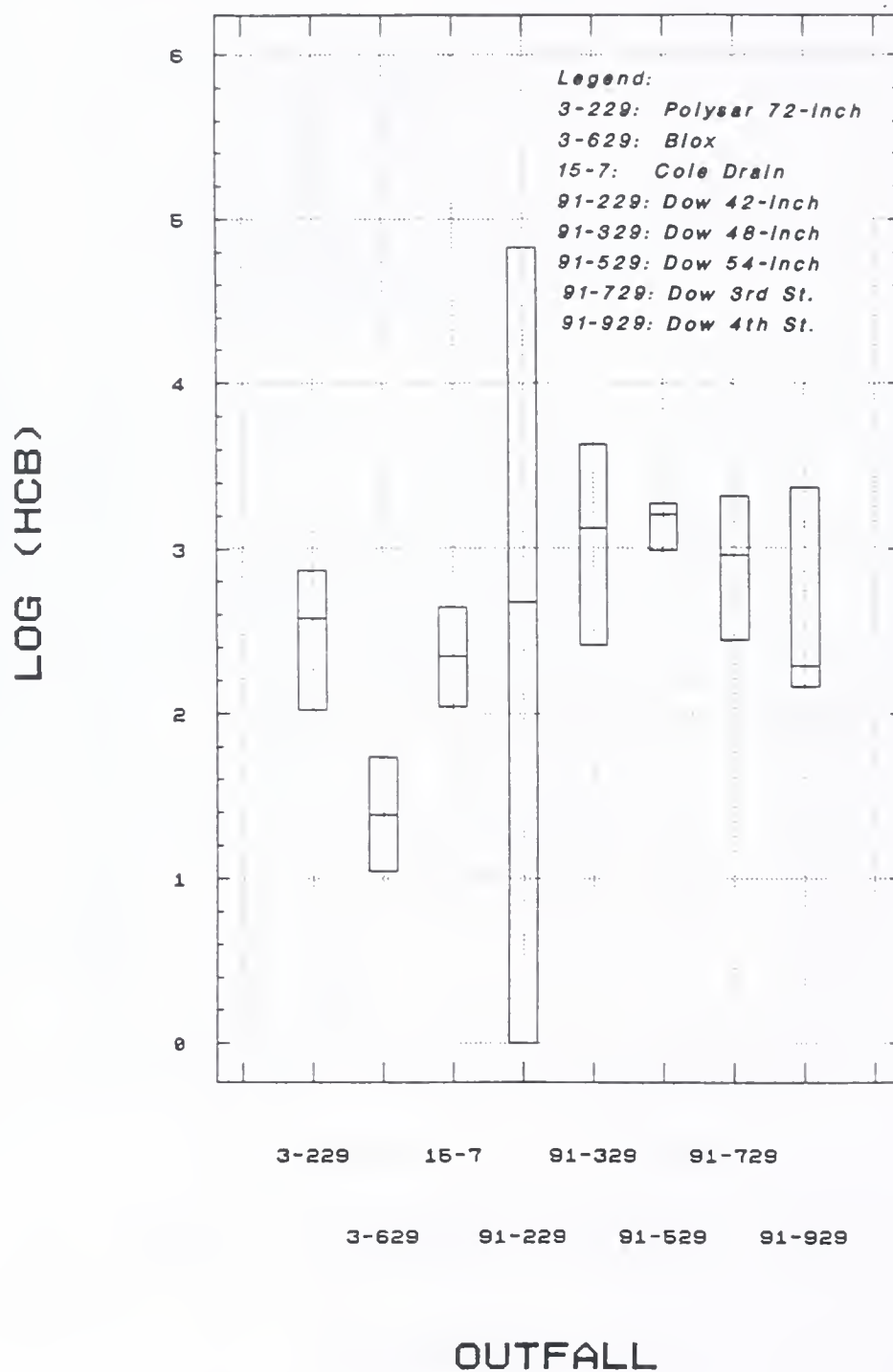


FIGURE 4.2.10

# 1,2,3,4-TCB ON SUSP. SOLIDS ANOVA BOXPLOT (95% C.I.)

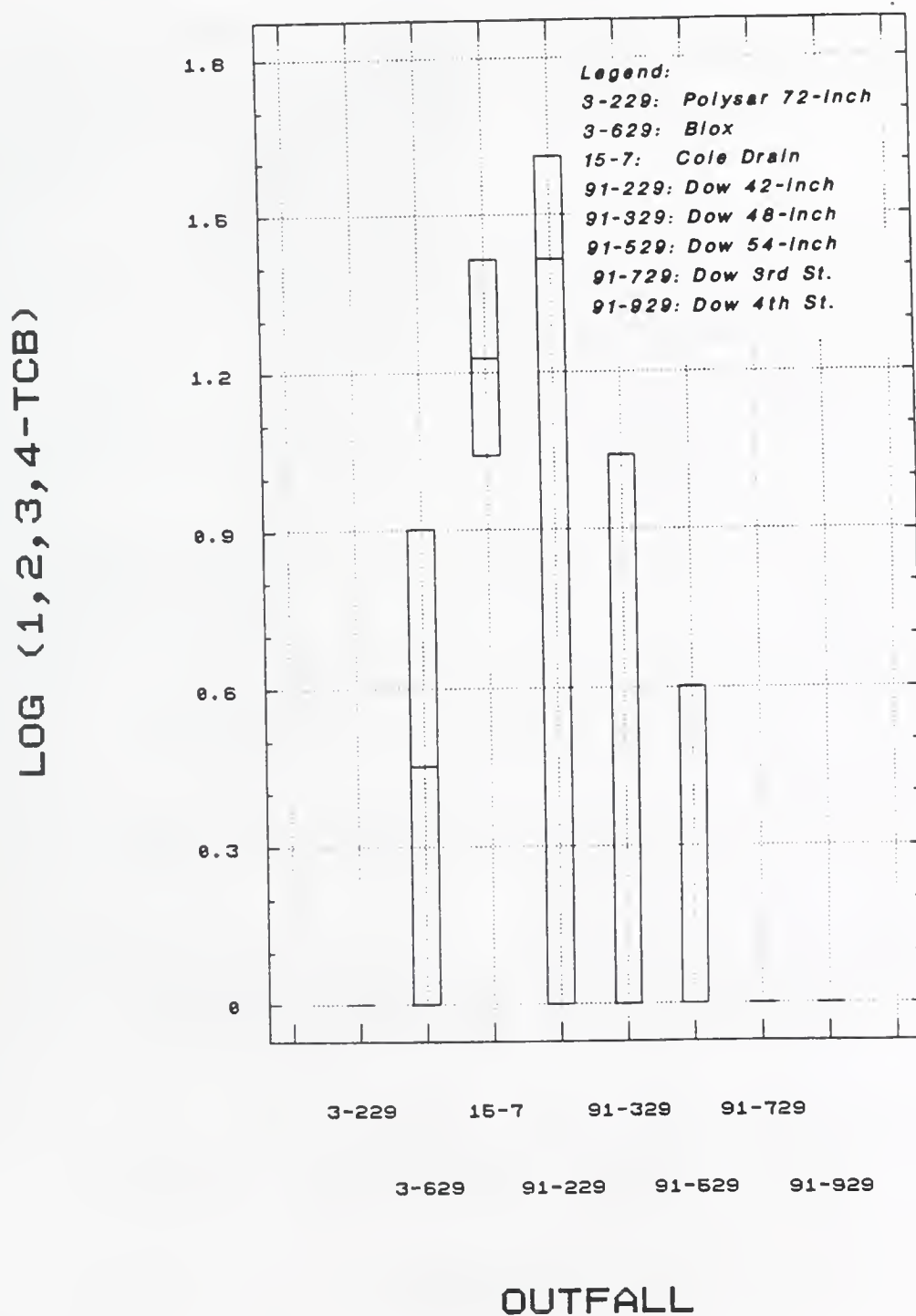
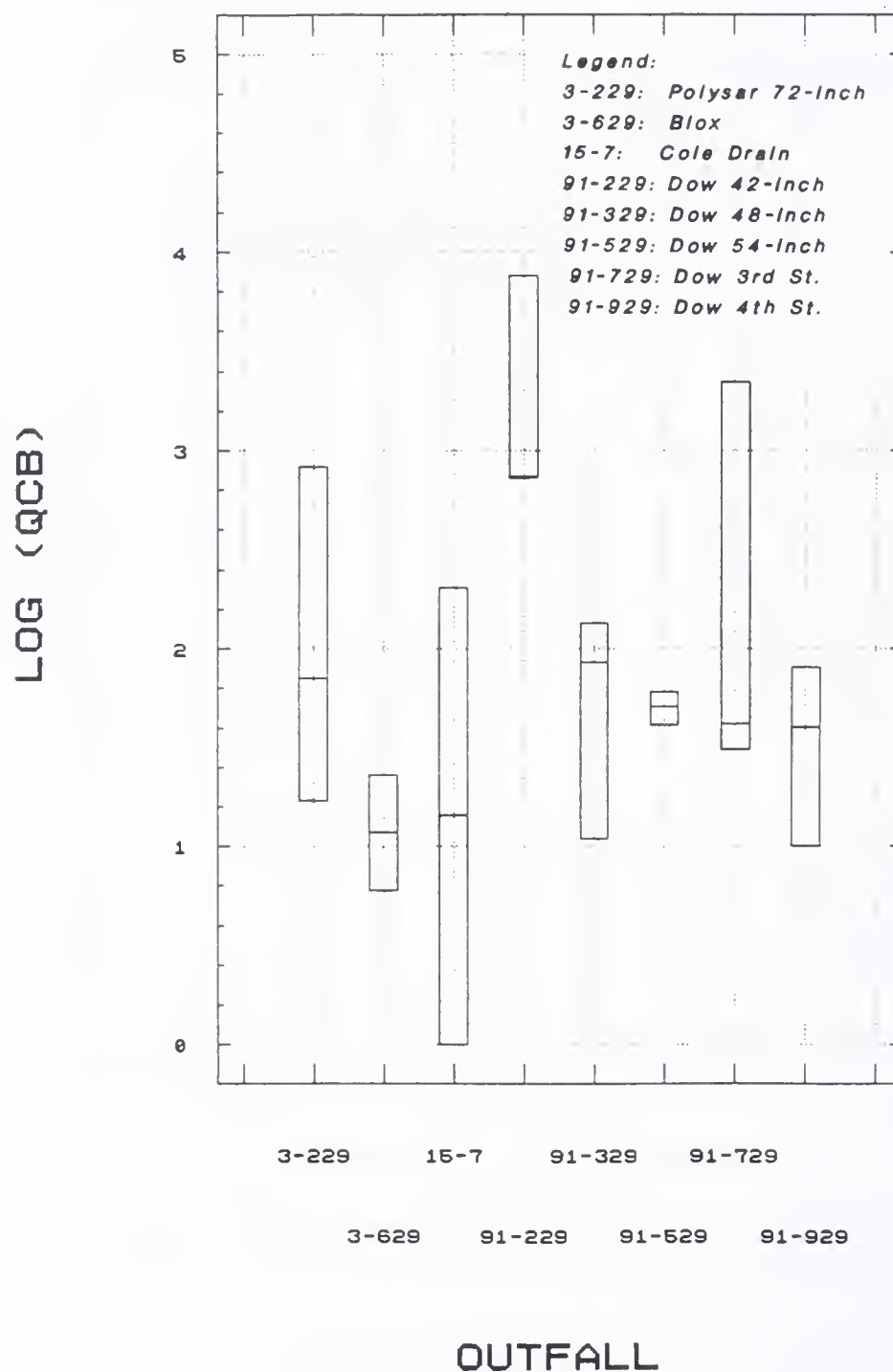


FIGURE 4.2.11

# QCB ON SUSPENDED SOLIDS ANOVA BOXPLOT (95% C.I.)





A vertical gradient was observed for Kjeldahl nitrogen, total phosphorus and pentachlorobenzene ( $p < 0.05$ ). Concentrations of the former 2 were highest 1.0 m subsurface, while pentachlorobenzene levels were highest in bottom waters.

Significant station effects were noted for HCB (D) ( $p < 0.0002$ ) following log transformation, as were depth effects ( $P < 0.04$ ). Both station and depth effects were noted following log transformation of HCB data.

Pooled results from each station provided further insight into spatial distribution independent of depth. Bottom and mid-depth averages from each station, and mid-depth samples from transects 25 and 214 were subjected to a 1-way ANOVA and a subsequent multiple range test (Tukey's). Significant differences between stations were noted for HCB, HCB and QCB (Figures 4.2.12 to 4.2.14).

Using the HCB results, it is seen that the measured concentrations within the river:

- (i) near the outfalls were well above the upstream river background values, (about 2 to 3 orders of magnitude),
- (ii) near Chenal Ecarte were approximately 1 order of magnitude lower than those near the outfalls, and
- (iii) on the U.S. side of the river across from Chenal Ecarte were about 1.5 times lower than those near Chenal Ecarte, but slightly above those of the river background.

This pattern is qualitatively similar to that revealed by the whole water sampling (eg. chlorides), and provides an indication of the 'zone of impact' within the river from discharged contaminants originating from the Cole Drain - Dow vicinity. It should be noted that quantitatively, the concentration ratios illustrated above will

differ for different contaminants. The major reason for this difference is that the ratio of total point source to upstream background loading rates will vary for the different contaminants.

There were no significant differences for mercury between upstream reference stations at the  $p < 0.05$  level; however, the spatial concentration gradient was arranged in ascending order from upstream to downstream stations.

A summary of findings following multiple range analysis is provided below:

PARAMETER	HCBD	HCB	QCB
Group 1	25US; 25C; 214US; 132	25US	25 US; 25C; 132; 214US
Group 2	214C	25C	214C; 218; 216
Group 3	218; 18; 203; 216; 206	132; 214US	211; 203; 18; 206
Group 4	211	214C; 216; 203	
Group 5		206	
Group 6		211; 218	
Group 7		18	

Contaminant concentrations increase with increasing Group numbers.

In general, the highest suspended sediment associated contaminant levels were noted at station 211 and 18 within the stretch of river immediately adjacent to Dow Chemical.

FIGURE 4.2.12

# HCBD ON SUSPENDED SOLIDS ANOVA BOX PLOT (95% C.I.)

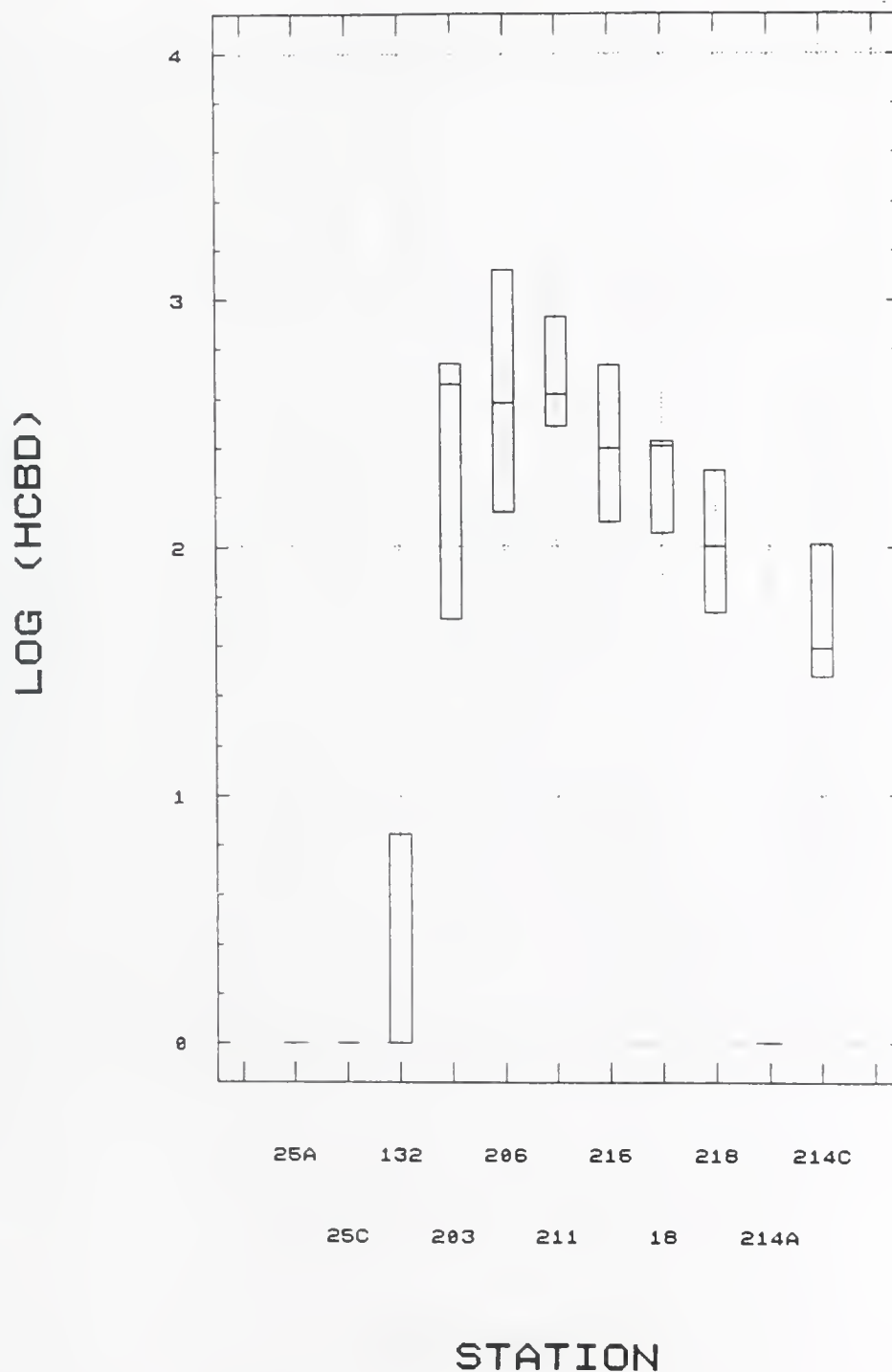


FIGURE 4.2.13

# HCB ON SUSPENDED SOLIDS ANOVA BOXPLOT (95% C.I.)

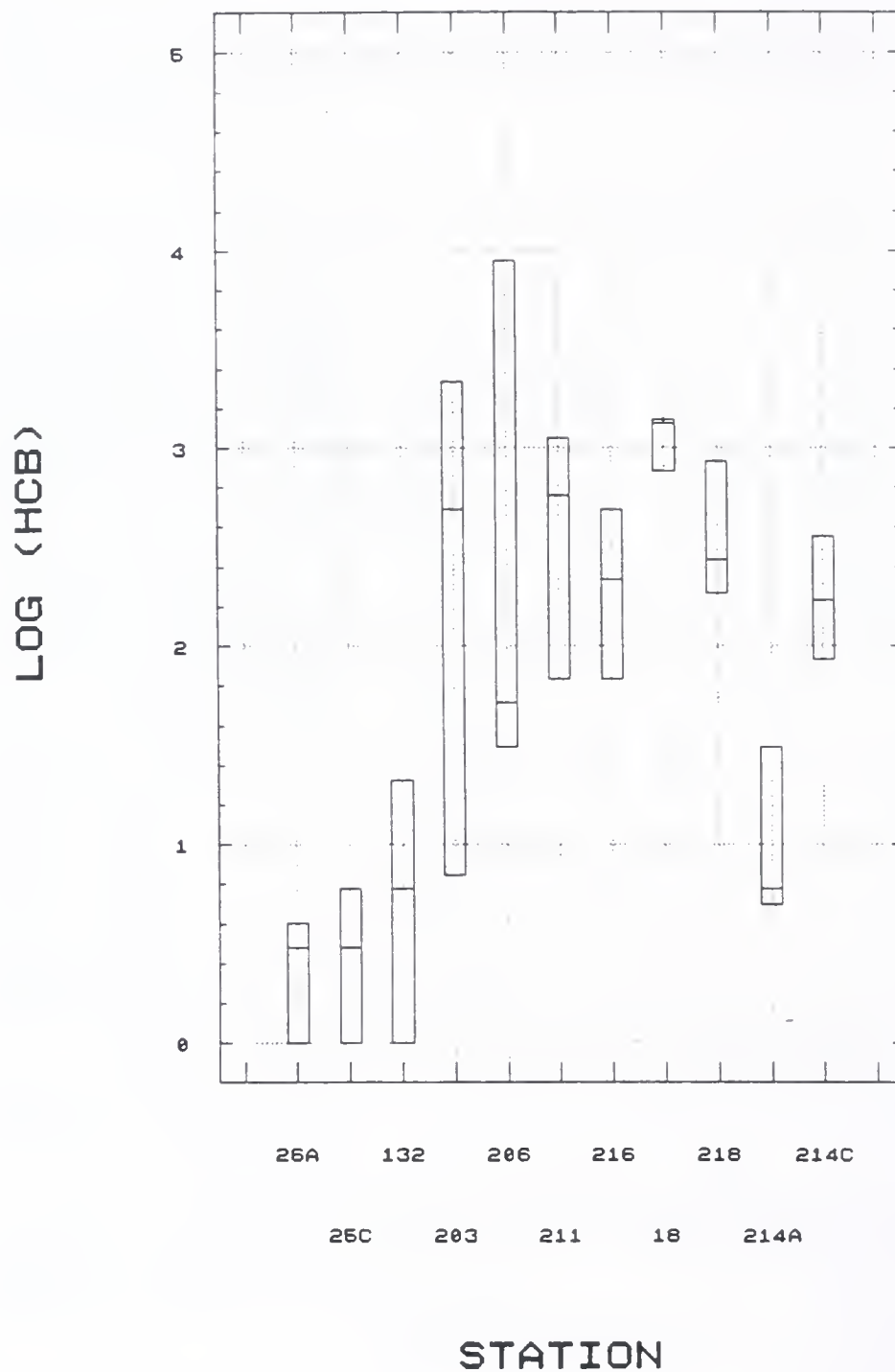
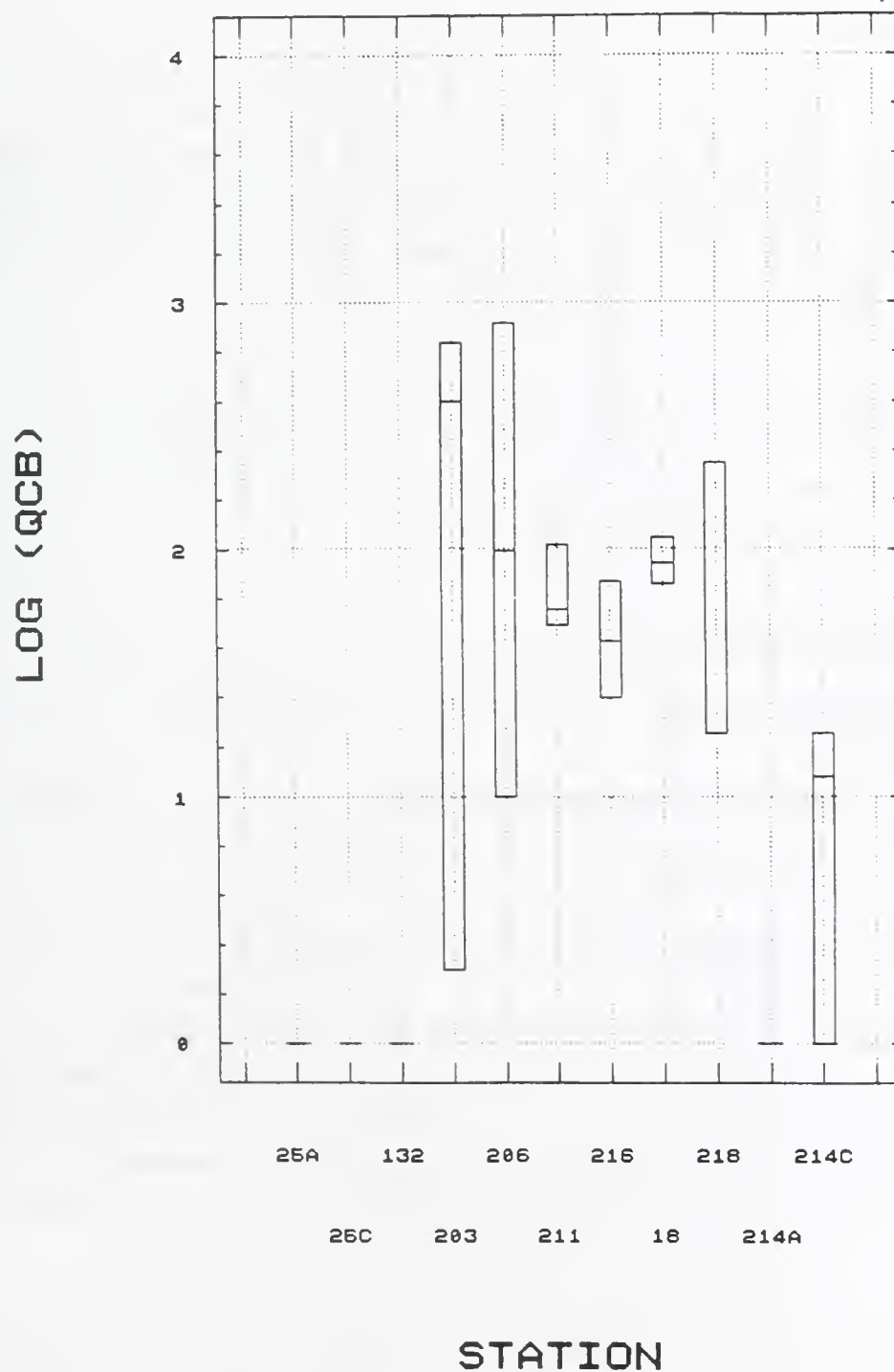


FIGURE 4.2.14

# QCB ON SUSPENDED SOLIDS ANOVA BOXPLOT (95% C.I.)



(d) Conclusions and Recommendations

Centrifugation is adequate for several purposes including identification and quantification of low level contaminants; however, these are tempered by extremely time intensive and costly sampling requirements.

To obtain a single sample, a vessel and/or truck is required. Two operators are necessary for the centrifuge unit itself and additional staff if a vessel is used. Time required to obtain an adequate sample is 6-8 hours with several hours additional dedicated to preparation before and after obtaining a sample.

The capital investment required to purchase a centrifuge and the necessary ancillary equipment is on the order of \$20,000 and up. Maintenance and repairs require specialized knowledge and parts/service are typically time consuming.

4.2.2 Investigative Water Sampling

(a) Introduction and Purpose

Several monitoring strategies were employed to document the spatial distribution of selected parameters throughout the St. Clair River.

By sampling surface and bottom water at 43 stations and sediments at approximately 50% of these locations, it was anticipated that point sources could be identified which emit specific process related compounds. It was further expected that the extent both laterally and downstream of point sources could be documented to identify the zone of potential impact. In addition, the extent of contamination at the water-sediment interface might provide additional information about contaminant transport and release in this thin microlayer.

This section of the report will focus on the water quality investigation by highlighting the occurrence and distribution of a number of parameters. Included, will be an assessment based on the compounds physical/chemical properties which may in part account for its distribution. To determine a chemicals significance in the environment, a brief comparison with existing water quality criteria/guidelines/objectives will also be undertaken.

While it is recognized that grab water samples provide only a snapshot perspective; the three cruises which were undertaken in this investigation should identify at least qualitatively, those compounds which are cause for concern, and from what source they are likely to originate. The results will further enable calibration and verification of near (close to source) and far field (distant from source) models for the prediction of the fate and transport of chemicals.

#### (b) Methods

Investigative sampling locations are listed in Table 4.2.4 and Figure 4.2.15. Forty-three stations were selected from the river headwaters to the St. Clair delta. These stations were typically situated at 10, 30 or 100m from the Ontario shoreline and as such encompass most shore based inputs (Hamdy and Kinkead 1979). Several stations were situated adjacent to the Michigan shoreline, thus determining the potential for trans-boundary chemical transport.

Grab water samples were obtained by divers (Cruise I - May 1986) and a teflon-lined submersible pump (Cruises II and III - July and October 1986) from within 0.2 m of the river bottom. Samples from 1.0 m subsurface were obtained by a custom fabricated stainless steel sampling basket into which bottles were inserted.

Cruises were undertaken during the periods May 26-29; July 14-17 and October 20-24, 1986. Samples were submitted for the parameters listed on Table 4.1.1 according to standard MOE sampling protocols (MOE



1985). Duplicate and blank samples were obtained at approximately 10% of the stations.

The detection limits for many chlorinated aromatic compounds was 1 ng/L (ppt) while volatile organic compounds were detectable above 1 µg/L (ppb).

(c) Results and Discussion

(i) Low Level Detection of Volatile Organic Contaminants

In many receiving environments with high initial dilution, such as the St. Clair River, volatile compounds cannot be quantified, particularly at current detection limits.

In order to adequately assess effluent impact by means of fate and transport models, it is essential that a numerical value be used instead of simply 'non-detectable'. This is a significant problem, particularly in the far-field.

During the MISA investigations, a need for a low detection limit for volatiles was evident, especially in the water column. This need is important to understand contaminant pathways in the ecosystem. The lack of numerical values for the concentrations of contaminants within the water-column, may potentially increase the level of uncertainty of predicted results used in developing the effluent criteria for MISA.

Being able to quantify low level concentrations will permit the calibration of dispersion, sediment-biota uptake, and water-air exchange coefficients for the fate and transport models. This is essential for effluent impact assessment.

In order to address this problem, the Laboratory Services Branch and the Water Resources Branch of the Ministry of the Environment with the assistance of an external consultant have jointly developed a method capable of determining selected volatile compounds at the low parts-per-trillion (ppt) level.

TABLE 4.2.4 - AMBIENT WATER INVESTIGATIVE SAMPLING LOCATIONS

STN.#	LOCATION	DISTANCE FROM CANADIAN SHORE (Reference Point)		WATER SURFACE    BOTTOM (Duplicate/Blank)	
25	SR 39.0; Head	100 m	(330 m)	x	x
25	SR 39.0; Head	366 m	( 60 m)	x	x
132	downstream CN Tunnel	30 m	( 0 m)	x	x
133	downstream CN Tunnel	30 m from US shore	( 0 m)	x	x
*202	SR 35.2	60 m	(460 m)	x	x
*202	SR 35.2	518 m	( 75 m)	x	x
22	SR 35.0 Adjacent to Cole drain	30 m	(545 m)	x	x
22	SR 35.0 Adjacent to Cole drain	100 m	(475 m)	x	x
203	10 m d/s of Cole drain Pipe	68 m	( 0 m)	x(x)	x(x)
119	SR 34.9	30 m	(540 m)	x	x
119	SR 34.9	100 m	(470 m)	x	x
116	SR 34.7 off Polysar Dock	10 m	(590 m)	x	x
116	" "	30 m	(570 m)	x	x
20	SR 34.4 Dow 1st Street	10 m	(550 m)	x(x)	x(x)
20	" "	30 m	(540 m)	x	x
20	" "	100 m	(470 m)	x	x
204	250 ft d/s of 1st St. sewers	10 m	( 0 m)	x	x
205	500 ft d/s of 1st St. sewers	30 m	( 0 m)	x	x
206	600 ft " "	10 m	( 0 m)	x	x
207	1000 ft " "	30 m	( 0 m)	x	x
208	1250 ft " "	10 m	( 0 m)	x	x
*201	SR 34.3 u/s of 2nd St. sewer	10 m	(650 m)	x	x
*201	SR 34.3 " "	30 m	(630 m)	x	x
*201	SR 34.3 " "	100 m	(560 m)	x	x
*201	SR 34.3 " "	533 m	(125 m)	x	x
209	At 2nd St.; 250 ft d/s of SR 34.3	10 m	( 0 m)	x(x)	x(x)
210	d/s of 3rd St.; 250 ft d/s of 209	30 m	( 0 m)	x	x
211	250 d/s of 210	10 m	( 0 m)	x	x
212	250 d/s of 211	30 m	( 0 m)	x	x
217	d/s of 4th St. sewer	10 m	( 0 m)	x(x)	x(x)
*216	SR 33.8	10 m	(590 m)	x	x
*216	SR 33.8	30 m	(570 m)	x	x
*216	SR 33.8	100 m	(500 m)	x	x
*216	SR 33.8	533 m	( 75 m)	x	x
18	SR 33.4	10 m	(635 m)	x	x
18	SR 33.4	30 m	(615 m)	x	x
18	SR 33.4	100 m	(545 m)	x	x
218	SR 31.1; d/s of Talfourd Ck.	100 m	(800 m)	x	x
*213	SR 33.4; d/s of Lambton Gen.Stn.	100 m	(467 m)	x	x
*213	" "	500 m	( 67 m)	x	x
009	SR 17.5; At Bluewater Ferry Crossing	200 m	(830 m)	x	x
*214	SR 12.9	120 m	(510 m)	x	x
*214	SR 12.9	550 m	( 80 m)	x	x

\* Samples submitted for regular parameter list plus major ions



A second and equally important consideration with respect to analysis for aqueous samples for volatile organic hydrocarbons is the need for a rapid turnaround time for a large number of samples. As a result, consideration of an automated method was incorporated into the analytical method.

To address both concerns, an ultra-clean automated system was selected utilizing the following methodology:

Water samples were purged with an inert gas. Purged organic compounds were subsequently collected in a packed sorbent cartridge. These cartridges were then loaded into an automatic thermal desorber and thermally desorbed into the gas chromatographic system.

Considering the low detection levels employed in this method, additional precautions had to be taken to minimize interferences which could hinder analyses.

For this analysis to perform as designed, it was necessary that equipment be operated in an ultra-clean environment using high purity gases with the appropriate moisture, oxygen and hydrocarbon traps in place.

Other potential sources of interference such as tobacco residues, hand creams, perfumes and laboratory solvents should be isolated from samples/equipment during analysis. It is recommended that a dedicated area with a separate ventilation system be designated.

Preliminary results indicated that samples which were stored on sorbent tubes could be kept refrigerated for at least 14 days with very little change. This appears to be a more suitable means of storage than the conventional glass bottle, and as such may benefit labs which experience some sample backlogs.

(ii) Spatial Contaminant Distribution in the St. Clair River

(a) Horizontal Distribution

A number of compounds which were measured in the St. Clair River were found at their highest levels adjacent to the "Chemical Valley" in Sarnia. A rapid dropoff was typically observed with increasing distance downstream as well as lateral distance from the Ontario shoreline.

The occurrence and concentration of chloride in whole water samples is in part from municipal water pollution control plants and urban runoff. Significant sources may also occur from the refinement of mined salt or in the manufacture of industrial chemicals. It is this latter source that accounted for elevated chloride concentrations at and downstream of the "Chemical Valley".

Typical background  $\text{Cl}^-$  levels at the St. Clair River headwaters vary from 5.8 to 7.1 mg/L (ppm). Inputs from sources such as the Cole drain (6.8-215 ppm range;  $\bar{x} = 71.6$  ppm) and the Dow 4th St. outfall (16.7-2050 ppm range;  $\bar{x} = 823$  ppm) contribute mean annual loadings of  $3.7 \times 10^6$  and  $1.4 \times 10^8$  kg respectively.

Chloride loadings from Ontario tributaries (Johnson and Kauss 1989) and municipal sources (Edwardson and King 1988) to the St. Clair River account for only 3.9 and 1.7% of the chloride loadings from these two point sources combined respectively.

As such, chloride may act as a useful indicator of the chemical dispersion of additional compounds with similar behaviour, originating from the near shore area in the Cole drain - Dow vicinity. However, this dispersion pattern will become progressively more difficult to distinguish travelling either downstream or away from the Canadian shore, since both 'interference' from other smaller sources and fluctuations in background concentrations will become relatively



larger (with respect to predicted levels from the Cole drain - Dow vicinity). Figure 4.2.16 presents a graphical representation of chloride concentrations measured in the St. Clair River. This figure represents mean values of surface and bottom samples obtained at the 43 station grid. The graphics package 'Surfer'<sup>TM</sup> was used to interpolate between measured points and produce a 3-dimensional view (not to scale) of chloride distribution.

A peak was observed at Station 203 immediately downstream of the Cole drain decreasing rapidly to only slightly above background levels adjacent to Dow Chemical. A second and higher peak occurred immediately downstream of the Dow 4th St. sewer at Station 217. Moving further downstream along the Canadian shoreline from here, a slow but steady drop-off occurred, with concentrations equalling about 8.8, 3.2, 1.8, 1.7, and 1.3 times the background level at the south boundary of Suncor, Talfourd Creek, Lambton Generating Station, Sombra, and Chenal Ecarte, respectively. These locations were approximately 1.0, 4.5, 17, 26, and 34 km, respectively, downstream of Dow's 4th Street sewer. This pattern is indicative of a lateral spreading of the plume within the river as it travels downstream. Upstream of Station 18 (near the south boundary of Suncor) the plume was contained within about 100m of the Canadian shore, as revealed by near background concentrations at this distance from shore.

The presence of minor point sources along the Michigan shoreline was indicated by a gradual increase with distance down river.

Similar behaviour was demonstrated for conductivity (Figure 4.2.17) with the exception that a slightly more pronounced overall increase was noted in the lower river.

Patterns for some industrial organic compounds were similar to chloride and conductivity. Several differences were apparent; however, in that the fall-off between the Cole drain and Dow Chemical outfalls was less evident, likely due to continuous elevated inputs from the Dow 1st St. complex.

FIGURE 4.2.16: CHLORIDE DISTRIBUTION  
IN THE ST. CLAIR RIVER (mg/L)

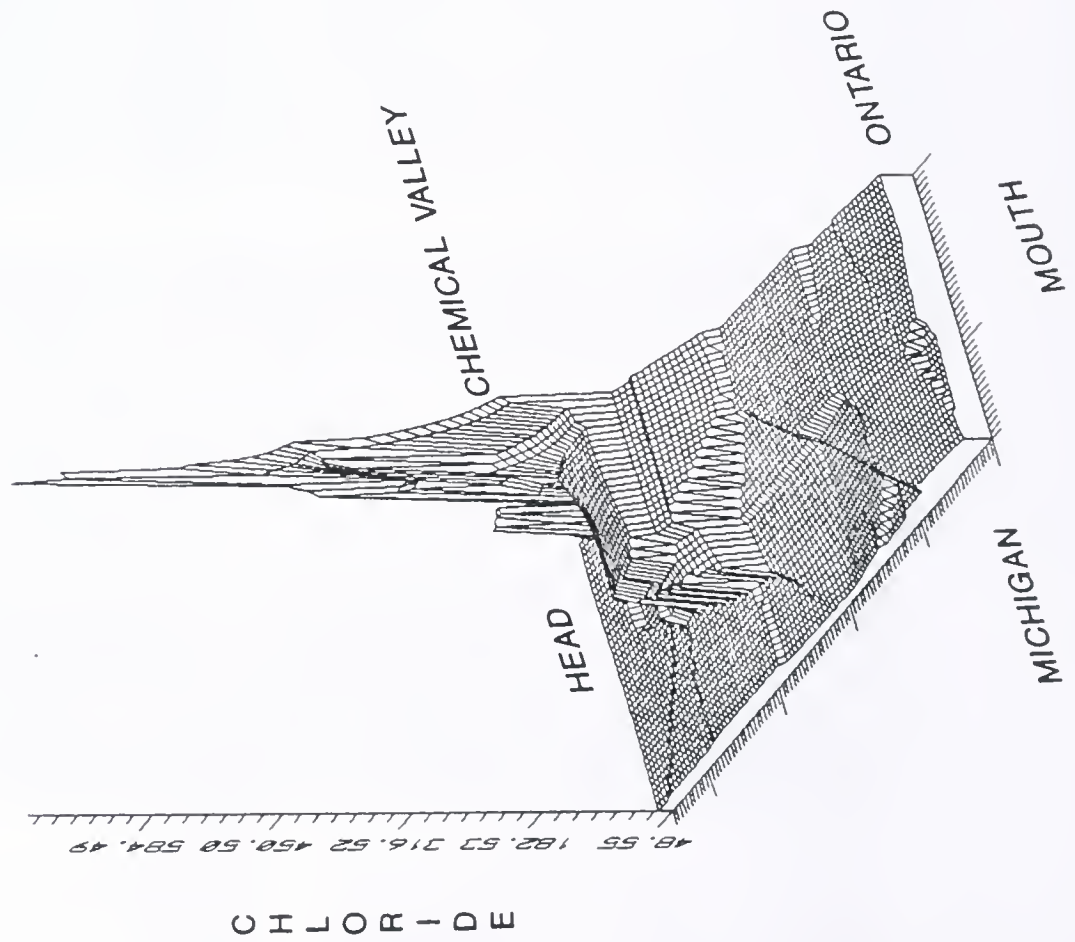
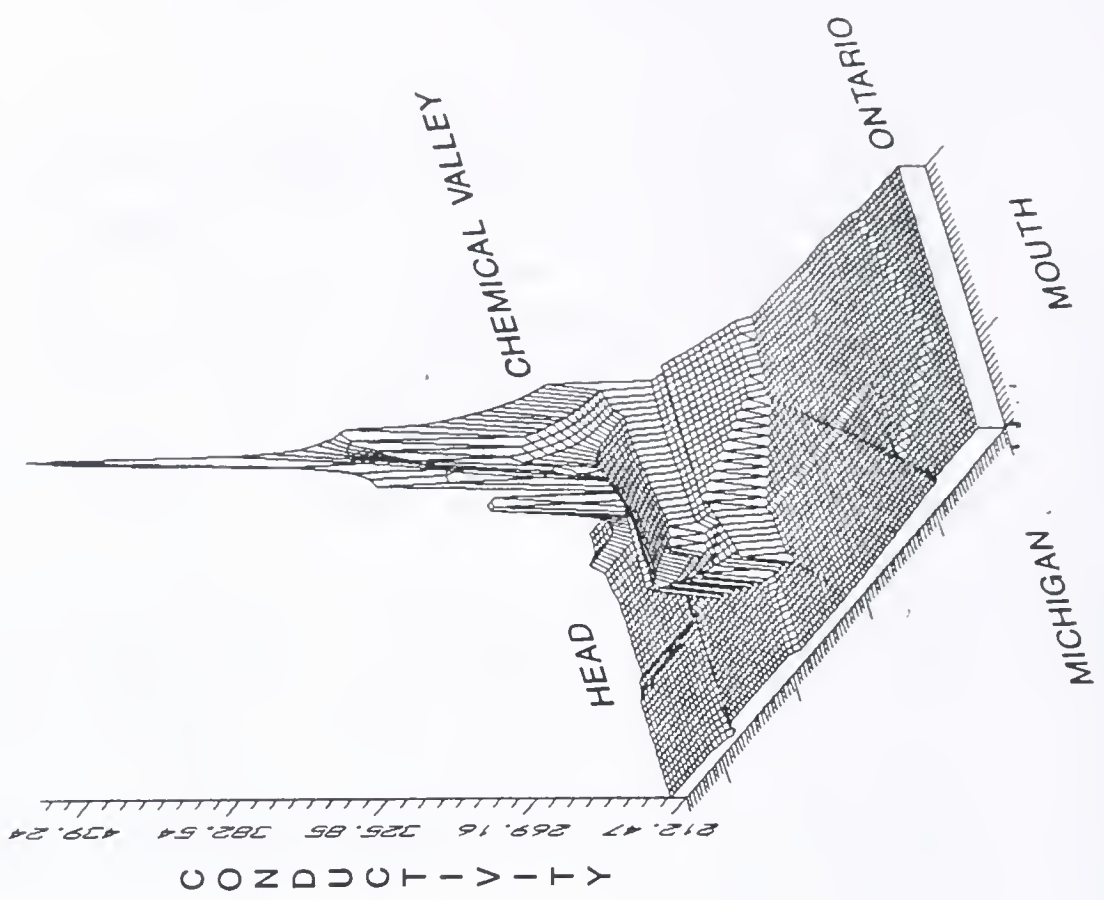


FIGURE 4.2.17: CONDUCTIVITY IN  
THE ST. CLAIR RIVER (umho/cm)





A further difference is the plateau or limit of detection which occurred at stations both upstream of sources and in the far field. This is a function of the analytical method which resulted in a lack of numerical values below the detection threshold. This is most evident for volatile organic hydrocarbons which have a method detection limit of 1 µg/L (1 ppb) versus 1 ng/L (ppt) for higher chlorinated hydrocarbons such as HCB and OCS. Figure 4.2.18 and Table 4.2.5 provide a summary of samples above detection limits by cruise for selected parameters. A summary of these criteria for a more complete list of parameters is provided in Table 4.2.6.

Figures 4.2.19 and 4.2.20 present findings for tetrachloroethylene and carbon tetrachloride respectively. One way analysis of variance (ANOVA) was conducted for all stations independent of depth for the above parameters. Both parameters exhibited significant differences between stations, which were further elaborated by multiple range analysis.

Stations 209, 204, 217 and nearshore stations on transects 20 and 201 represented a single homogenous group, while the highest station by far was the station 30m from shore along transect 20.

The distribution of tetrachloroethylene as presented in Figure 4.2.19, revealed an abrupt drop in concentration both laterally and in the downstream direction. Two concentration gradients emanated from the shore adjacent to the Dow 1st St. complex. One extended offshore beyond the sampling location situated 100m from shore, while downstream effects were noted in only a very narrow band adjacent to shore. Concentrations at the southern Dow property line and downstream from this point were at or below the MDL of 1 µg/L. Water quality objectives for tetrachloroethylene established by the Canadian Council of Resource and Environment Ministers (CCREM 1987) and the World Health Organization (WHO) are 260 and 10 µg/L respectively. The former value is recommended for the protection of aquatic life, while the WHO value is for the protection of human health based on a predetermined cancer risk of  $1 \times 10^{-5}$ . Of 284 samples obtained from the St. Clair River, 10 were above the WHO guideline. All of these samples were obtained adjacent to Dow property.

TABLE 4.2.5: SAMPLES EXCEEDING WATER QUALITY CRITERIA FOR SELECTED PARAMETERS BY SURVEY

% > W Q O				
	PWQO µg/L	May (n)	July (n)	October (n)
HCB	0.0065*	9.4 (9/85)	14.9 (14/94)	9.8 (9/92)
HCE	13 <sup>1</sup>	1.1 (0/85)	0 (0/94)	0 (0/92)
CCL4	27 <sup>1</sup>	1 (1/94)	1 (1/95)	0 (0/93)
PERC	260 <sup>2</sup>	0 (0/94)	0 (0/95)	0 (0/95)
HCBD	0.1 <sup>2</sup>	0 (0/85)	0 (0/94)	2.2 (2/92)

\* - Ontario Ministry of the Environment, Provincial Water Quality Objective (PWQO) for the protection of Aquatic Life.

1 - Michigan Department of Natural Resources guideline for the protection of Aquatic Life.

2 - Canadian Council of Resource and Environment Ministers (CCREM) guideline for the protection of Aquatic Life.

TABLE 4.2.6: FREQUENCY OF SAMPLES IN EXCESS OF METHOD DETECTION LIMITS (MDL) AND WATER QUALITY CRITERIA (WQC)

PARAMETER	MDL	WQC µg/L	%>MDL	%>WQC	N	MIN.	MAX.	X̄
					see "MDL" for units			
BENZENE	1 µg/L	300 <sup>3</sup>	0	0	283	0	0	0
TOLUENE	"	300 <sup>3</sup>	0	0	284	0	0	0
ETHYLBENZENE	"	700 <sup>3</sup>	0	0	284	0	0	0
XYLENE - m, p	"	N.A	0	-	284	0	0	0
1,1,2-TRICHLOROETHANE	"	N.A	2.8	-	284	0	4	0.1
XYLENE - o	"	N.A	0	-	284	0	0	0
ALDRIN	1 ng/L	.001 <sup>1</sup>	0	0	271	0	0	0
ALPHA - BHC	"	.01 <sup>1</sup>	95.6	0	271	0	5	2.5
GAMMA - BHC	"	.01 <sup>1</sup>	16.2	0	271	0	5	0.4
DIELDRIN	"	0.001 <sup>1</sup>	0.4	.4	271	0	2	0.01
HEPTACHLOR	"	0.01 <sup>2</sup>	7.0	0	271	0	7	0.3
CARBON TETRACHLORIDE	"	27 <sup>2</sup>	25.5	.4	282	0	42	0.8
HEXACHLOROBENZENE	1 ng/L	.0065 <sup>1</sup>	42.8	11.8	271	0	210	4.4
TETRACHLOROETHYLENE	1 µg/L	260 <sup>3</sup>	32.8	0	284	0	44	1.5
HEXACHLOROETHANE	1 ng/L	13 <sup>2</sup>	26.6	0	271	0	169	3.1
OCTACHLOROSTYRENE	"	0.0001 <sup>4</sup>	7.8	7.8	271	0	20	0.4
PENTACHLOROBENZENE	"	0.03 <sup>3</sup>	10.0	0	271	0	13	0.4
2,4,5-TRICHLOROTOLUENE	"	0.117 <sup>4</sup>	3.7	0	271	0	86	1.2
1,2,3,4-TETRACHLORO- BENZENE	"	0.1 <sup>3</sup>	3.3	0	271	0	7	0.1
1,2,4-TRICHLOROBENZENE	"	0.5 <sup>3</sup>	3.3	0	271	0	179	1.7
HEXACHLOROBUTADIENE	"	0.1 <sup>3</sup>	46.4	0.1	271	0	116	6.5

<sup>1</sup> - MOE Provincial Water Quality Objective (PWQO) for the protection of aquatic life

<sup>2</sup> - Michigan Department of Natural Resources (MDNR) Guideline for aquatic life

<sup>3</sup> - Canadian Council of Resource and Environment Ministers (CCREM) Guideline for the protection of aquatic life

<sup>4</sup> - MOE Water Quality Advisory (conservative number based on limited toxicological information) - Note: Value for 2,4,5 - Trichlorotoluene has been since updated to 0.134 based on additional information.

**FIGURE 4.2.18 : Frequency of samples above Method Detection Limits (MDL)**

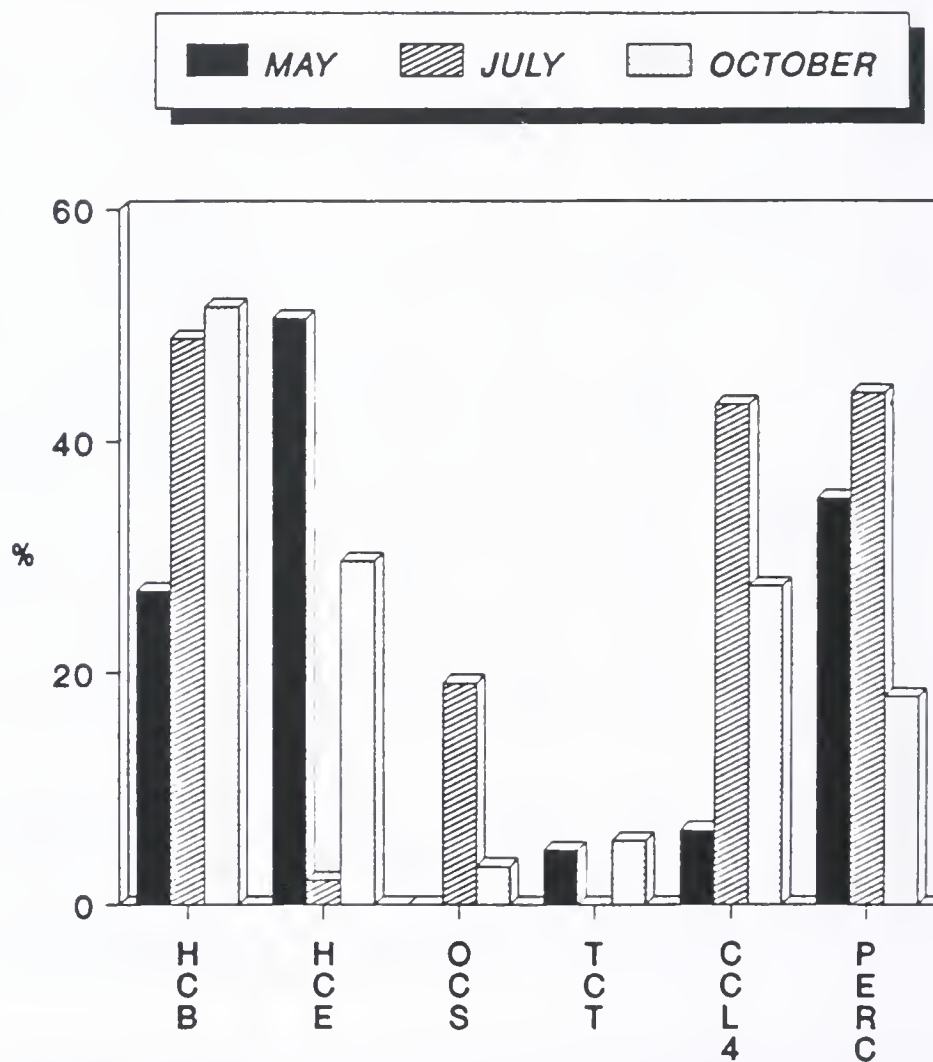


FIGURE 4.2.19 TETRACHLOROETHYLENE  
DISTRIBUTION IN THE ST. CLAIR RIVER  
(ug/L)

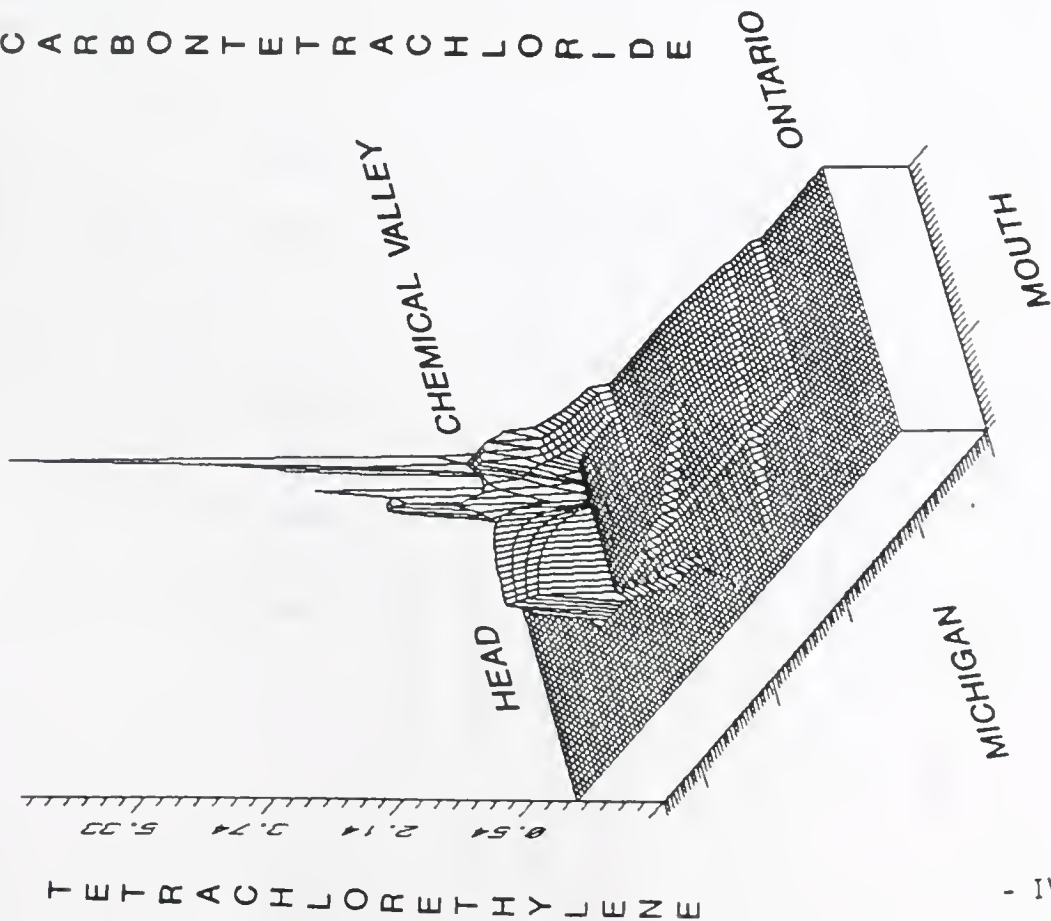
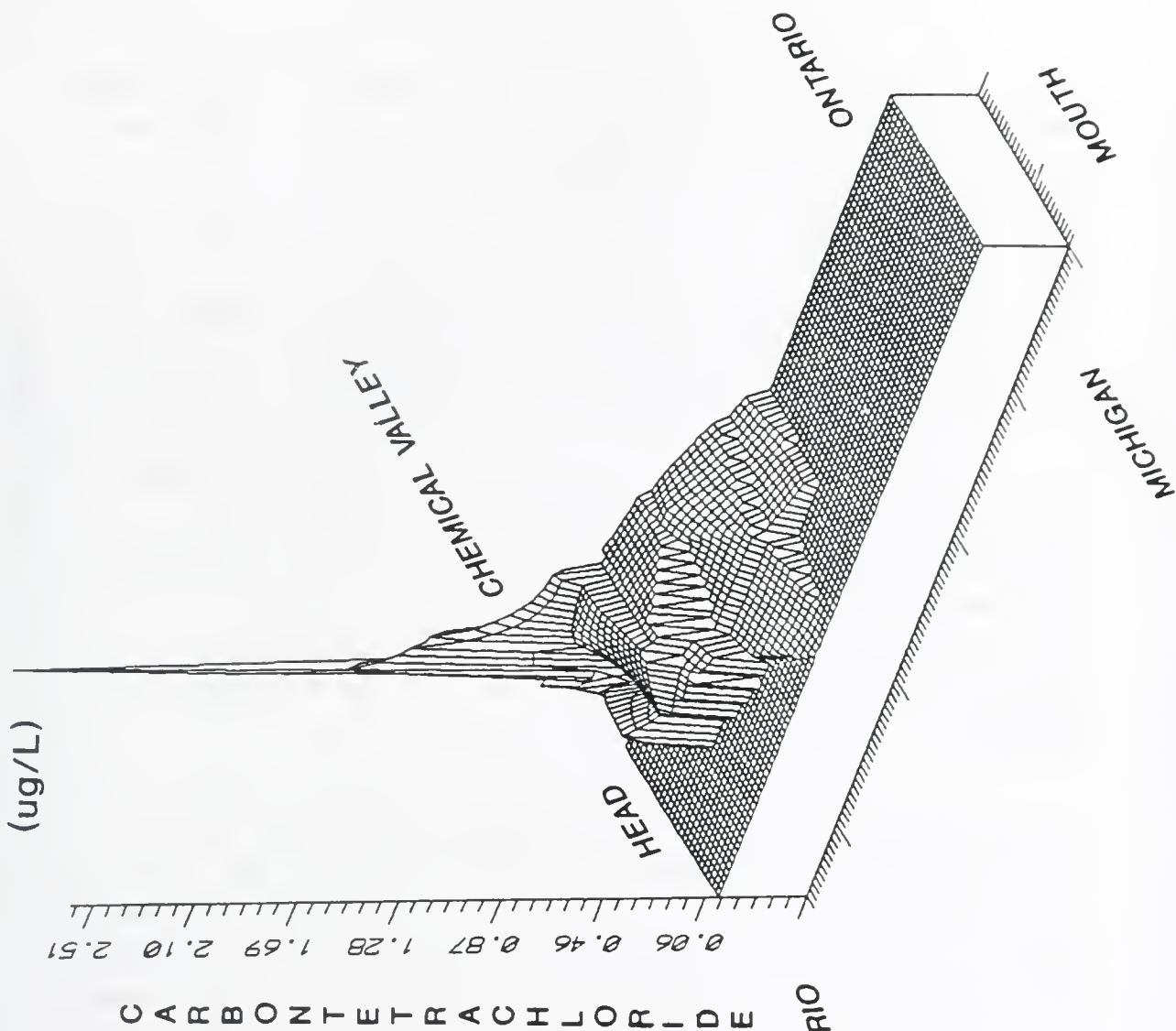


FIGURE 4.2.20: CARBON TETRACHLORIDE  
DISTRIBUTION IN THE ST. CLAIR RIVER  
(ug/L)





As indicated in Table 4.2.7 the majority of samples exceeding the WHO guideline were obtained during the July 14 - 17 period. Coincident effluent sampling for the Dow 42-inch sewer revealed a mean tetrachloroethylene concentration of 68 µg/L, twice the overall mean of 34 µg/L for the 10 month period monitored. Effluent concentrations measured during the May 26 - 29 period and immediately preceeding the October 20 - 23 period were 0 and 33 µg/L respectively demonstrating the cause/effect relationship between the outfall and receiver.

The Michigan Department of Natural Resources have endorsed a water quality objective of 27 µg/L for carbon tetrachloride for the protection of aquatic life. While this objective was not exceeded in 282 samples, a larger proportion were above the MDL than for tetrachloroethylene. This latter fact is reflected in the more wide ranging distribution, perhaps due in part to a higher solubility of 800 µg/L.

Figures 4.2.21 - 4.2.23 depict the depth-averaged concentrations of HCB, OCS and HCE. Peak concentrations were very localized with a relatively rapid depuration. While only a tentative MOE water quality advisory exists for OCS, criteria exist for HCB (6.5 ng/L - MOE) and HCE (13 µg/L-MDNR). The frequency of exceedance for these parameters is outlined in the Table 4.2.6. Hexachlorobenzene levels were determined in excess of the PWQO at station 119, downstream of the Cole drain outfall, and again at several stations downstream of the Dow 1st St. outfalls. Concentrations downstream of the Dow property line (1.1 km below 1st St. complex) were not in violation of the objective.

The above measurements contrast sharply with observations in 1984 and 1985 (DOE/MOE 1986). HCB levels in 1984 averaged 400 ng/L (n = 7) with a maximum concentration of 2.4 µg/L, at a point 100m downstream of the Dow 1st St. complex. At a distance of 600m downstream from this source, levels were still in excess of the PWQO by a factor of 100 indicating that simple dilution is not an appropriate alternative to treatment.

TABLE 4.2.7 - SAMPLES MEASURED ABOVE DETECTION LIMITS FOR SELECTED PARAMETERS BY CRUISE AND DEPTH

PARAMETER	MDL μg/L	MAY 26-29, 1986			JULY 14-17, 1986			OCTOBER 20-23, 1986		
		% > MDL			% > MDL			% > MDL		
		OVERALL (n)	SURFACE	BOTTOM	OVERALL (n)	SURFACE	BOTTOM	OVERALL (n)	SURFACE	BOTTOM
HEXACHLOROBENZENE	0.001	27.1(85)	16.3	38.1	48.9(94)	36.2	61.7	51.1(92)	37.8	63.8
HEXACHLOROBUTADIENE	0.001	47.1(85)	34.9	59.5	46.8(94)	42.6	51.1	42.4(92)	35.5	48.9
HEXACHLOROETHANE	0.001	50.6(85)	39.4	61.9	2.1(94)	2.1	2.1	29.3(92)	31.1	27.7
OCTACHLOROSTYRENE	0.001	0(85)	0	0	19.1(94)	10.6	27.7	3.3(92)	4.4	2.1
2,4,5-TRICHLOROTOLUENE	0.001	4.7(85)	6.98	4.8	0 (94)	0	0	5.4(92)	4.4	6.4
CARBON TETRACHLORIDE	1.0	6.4(94)	8.5	4.3	43.2(95)	46.8	39.6	26.9(93)	33.3	20.8
TETRACHLOROETHYLENE	1.0	35.1(94)	34.0	36.2	44.2(95)	46.8	47.9	17.9(95)	19.2	16.7



FIGURE 4.2.21: HEXACHLOROBENZENE  
DISTRIBUTION IN THE ST. CLAIR RIVER  
(ng/L)

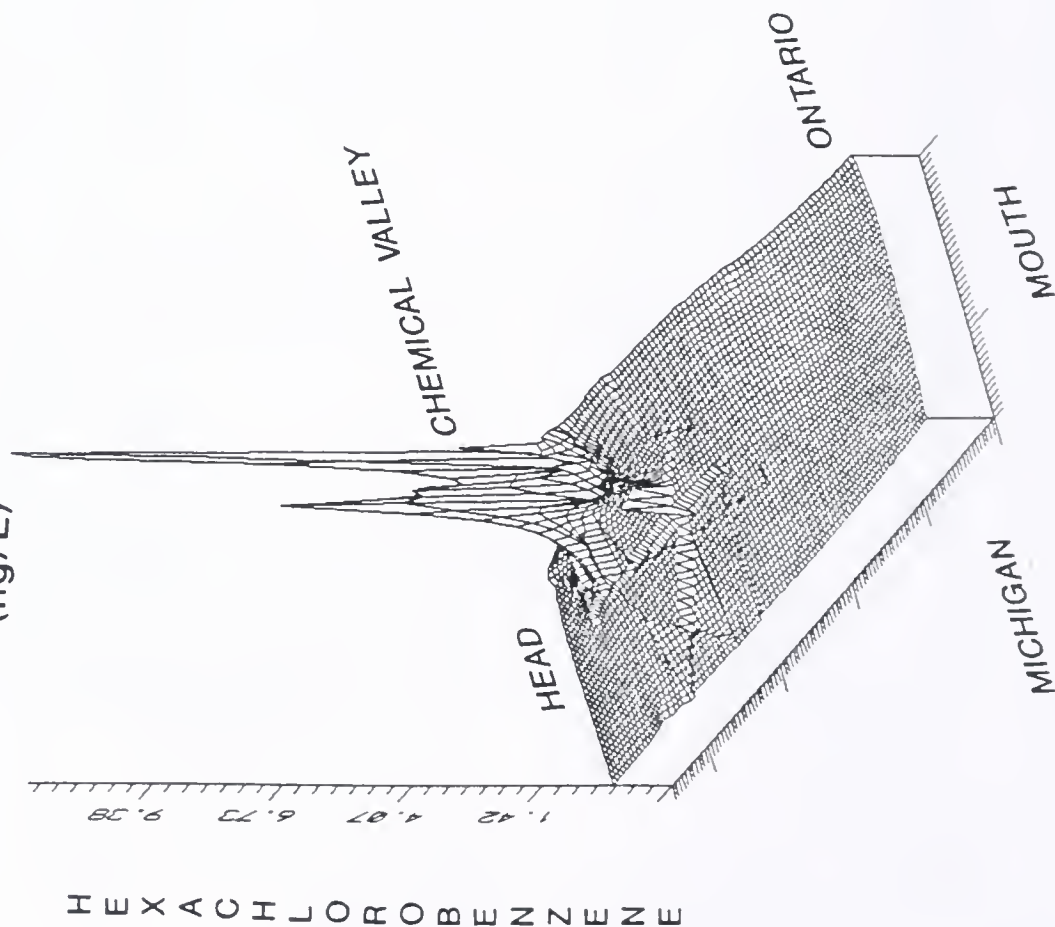


FIGURE 4.2.22: OCTACHLOROSTYRENE  
DISTRIBUTION IN THE ST. CLAIR RIVER  
(ng/L)

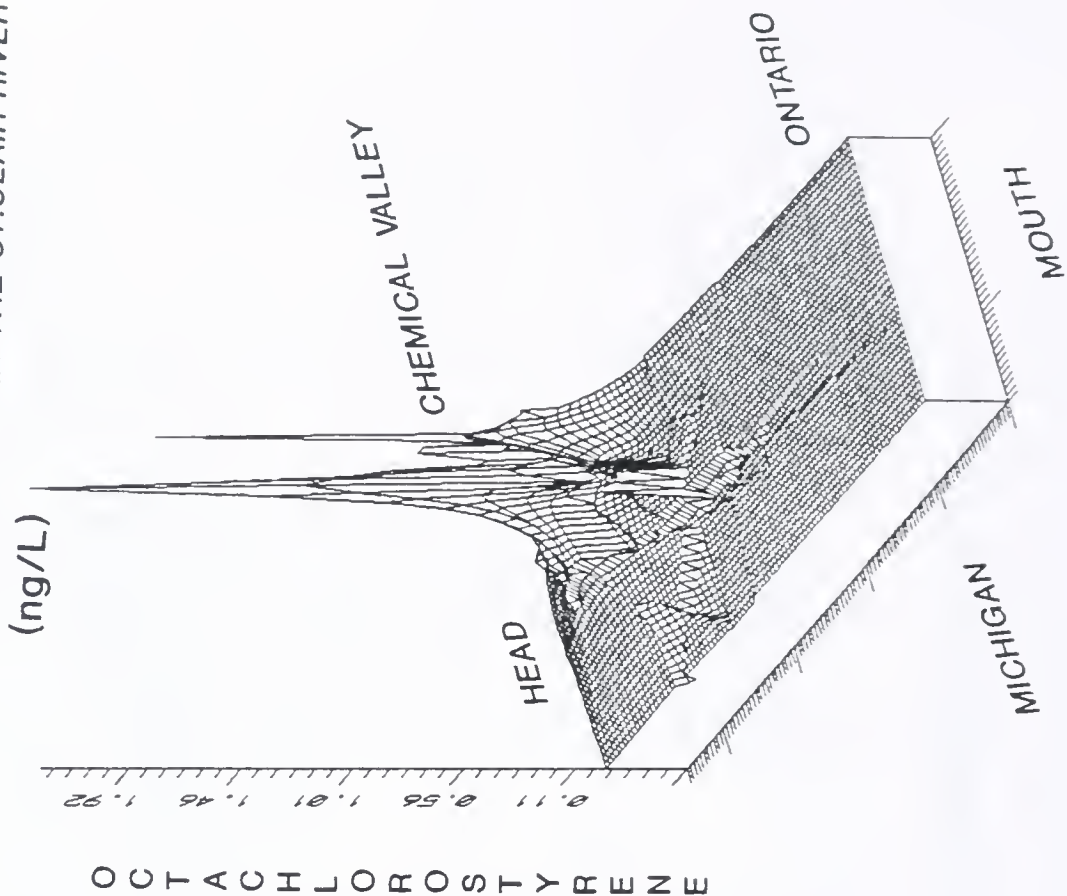
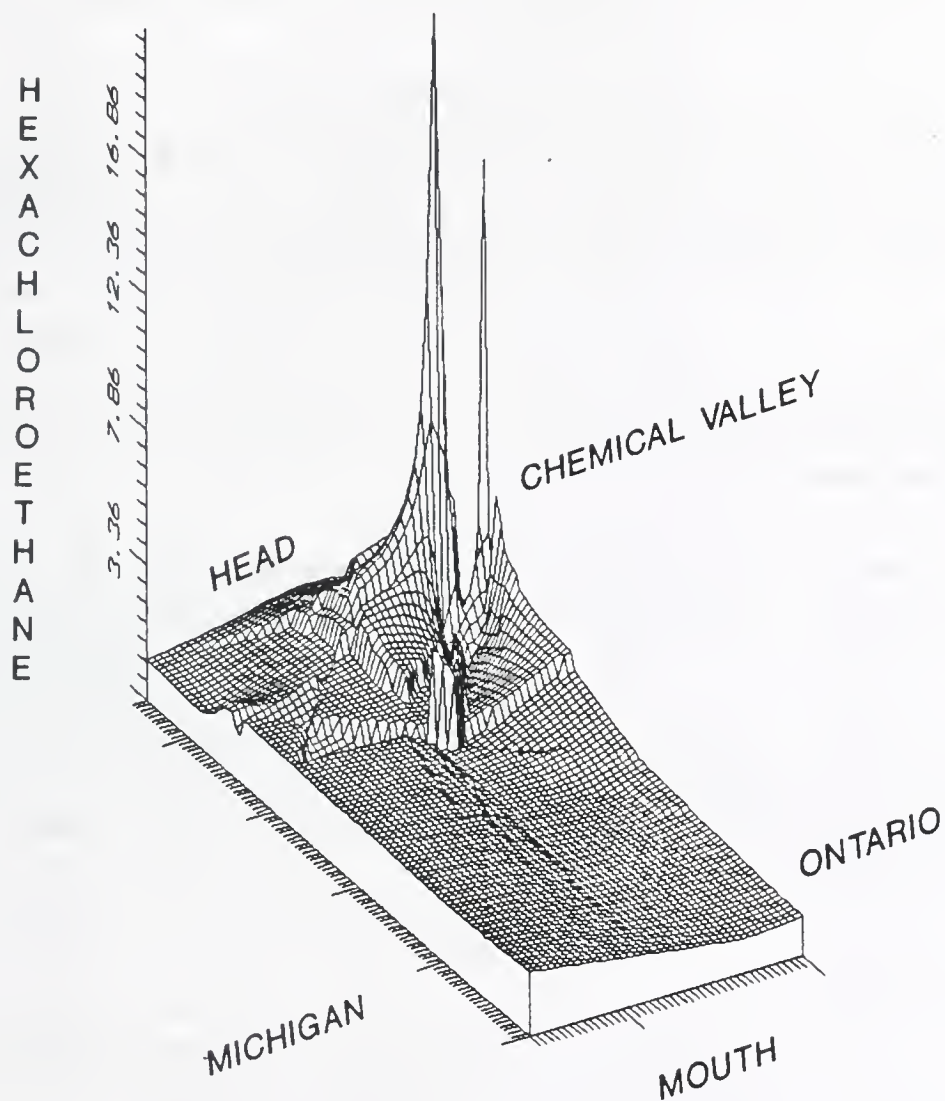


FIGURE 4.2.23: HEXACHLOROETHANE  
DISTRIBUTION IN THE ST. CLAIR RIVER (ng/L)



While concentrations during November 1985 had decreased since 1984, a peak concentration of 131 ng/L was observed. The PWQO was exceeded as far downstream as the head of Stag Island near Corunna (DOE/MOE 1986).

Octachlorostyrene is a highly persistent and bioaccumulative substance; however, there is insufficient information to determine if it has carcinogenic potential (HSDB 1987; CESARS 1989). It has been flagged as a chemical of potential concern due to its above characteristics and its documented presence in some Ontario surface waters.

The distribution of OCS was similar in nature to HCB; however, mean concentrations were typically one-fifth of those observed for HCB. Of 271 samples approximately 7.7% (21) were above method detection limits (1 ng/L) and therefore above the MOE advisory.

The occurrence of hexachlorobutadiene (HCBd) was not unlike HCB. One exception was noted for station 119, downstream of the Cole drain at which HCBd concentrations ranged from 53 to 116 ng/L. The high value in excess of existing water quality criteria occurred during October and likely reflects inputs from the Cole drain. Loading estimates from twice-weekly effluent monitoring indicated that the Cole drain loses approximately 140 g/day of HCBd, a five-fold increase over loadings from the Dow 42-inch sewer.

#### (b) Vertical Distribution

Table 4.2.7 provides a summary of samples exceeding method detection limits for selected parameters by cruise and depth. For most parameters, there appeared to be relatively uniform vertical distribution based on a comparison of surface (1m sub-surface) and bottom (within 20 cm of bottom) water samples.

Several factors may affect this distribution, in particular the temperature difference ( $\Delta t$ ) between the receiving water and industrial discharges as well as specific chemical properties. These may include specific gravity, solubility, vapour pressure, and partitioning coefficients.

Parameters such as carbon tetrachloride and tetrachloroethylene with solubilities of 800 and 150 µg/L respectively should disperse relatively rapidly throughout the water column. This was generally observed and was particularly evident during the July cruise when ambient and effluent temperatures were similar. During May and October, the effluent temperature exceeded the receiving water, resulting in a buoyant plume and consequently, more contaminants associated with the surface samples. This was more evident at nearfield locations and became less significant as mixing occurred further downstream.

Compounds such as HCB and OCS are hydrophobic and readily adsorb to particulate material in suspension. This factor, coupled with a high specific gravity as measured for HCB (2.044 - CESARS 1989) may have resulted in deposition of newly discharged material or resuspension of historical deposits and a concomitant elevation in bottom water concentrations.

2,4,5-trichlorotoluene (2,4,5-TCT) is insoluble in water and soluble in many organic solvents and was therefore only occasionally detected in whole water samples. Resuspension did not likely contribute to contamination of the water column, as sediment samples from the 1st St. vicinity did not contain this material. Interestingly, suspended solids removed through centrifugation also did not contain any detectable amounts even though it was readily detected in effluent samples; however, the absence of 2,4,5-trichlorotoluene may be explained by the fact that it hydrolyzes to benzoic and hydrochloric acids in the presence of water (Merck 1968).

### 4.3 Contaminants in the St. Clair River Sediments

#### 4.3.1 Sediment Contaminant Distribution

##### (a) Introduction

The recent severe contamination of the St. Clair River by chemicals originating from industrial activities, in the area around Sarnia, has been documented (DOE/MOE 1986, MOE 1987). The concentrations of many chlorinated hydrocarbons have been measured in whole water, and suspended and bottom sediments taken from the St. Clair River. The sediment data pinpointed major sources of contamination in the Sarnia industrial area, and demonstrated widespread downstream contamination to Lake St. Clair (Oliver and Pugsley 1986, DOE/MOE 1986). High concentrations of mercury have also been found in bottom sediments collected from the St. Clair River near Sarnia. The concentration profiles of mercury in Lake St. Clair sediment cores indicated continuous input of this element into the lake (Mudroch and Hill 1987).

This section contains information pertaining to contaminants in the St. Clair River sediments obtained in 1986 by the Ontario Ministry of the Environment. The results were interpreted with the objective of assessing the techniques used to obtain sufficient information for the establishment of effluent regulations.

##### (b) Methods

###### (i) Sampling Technique

Bottom sediments were sampled using a Shipek grab sampler during a cruise in the St. Clair River in October 1986. Duplicate sediment samples were collected at 23 sampling stations (Figure 4.3.1). Individual sediment samples were mixed by a pre-rinsed stainless steel stirrer and divided into several containers for analysis.



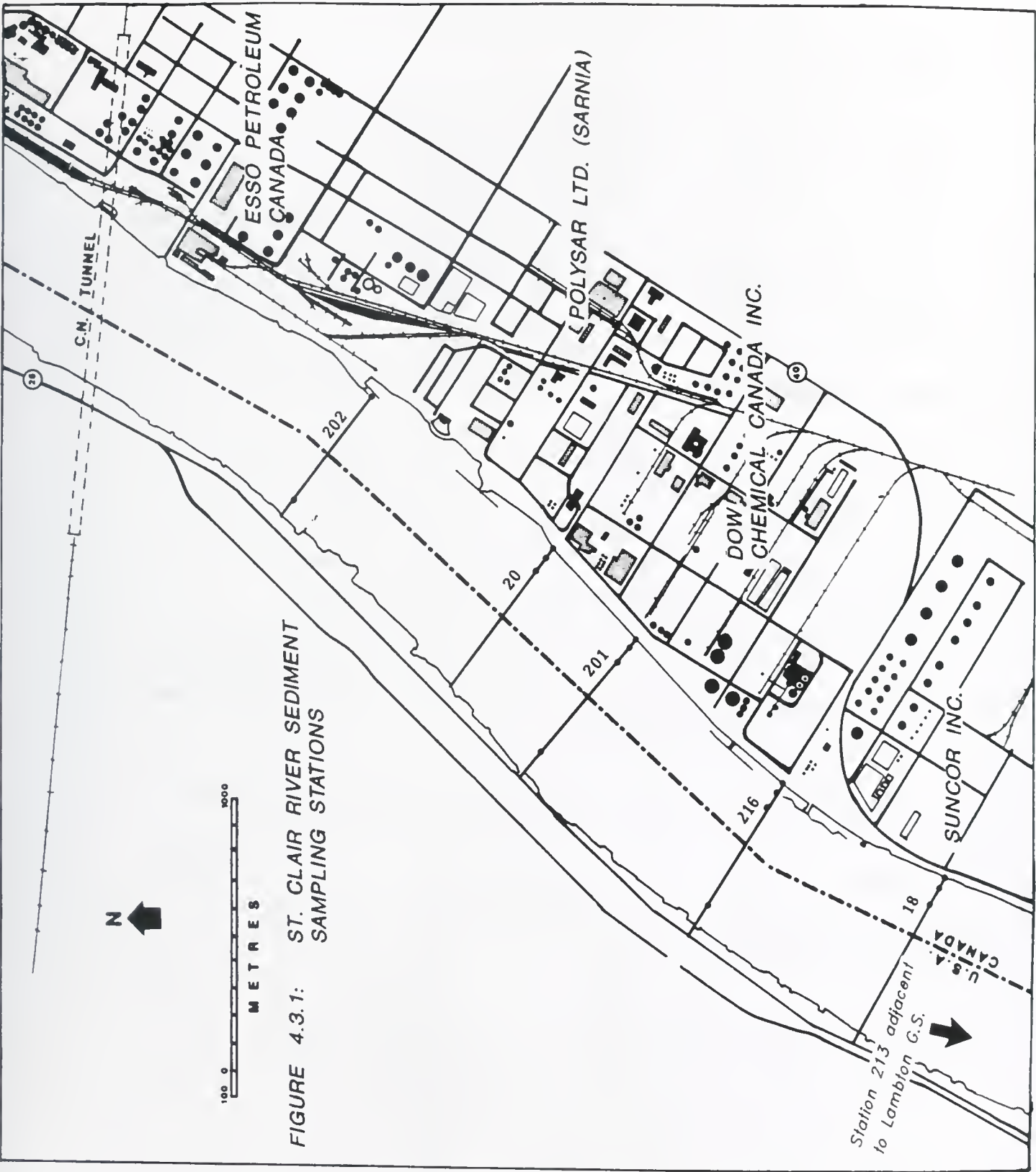


FIGURE 4.3.1: ST. CLAIR RIVER SEDIMENT SAMPLING STATIONS

## (ii) Sample Preservation

Solvent-rinsed glass jars were used for the determination of chlorinated organics; plastic jars for the determination of metals, nutrients, organic matter and particle size distribution; glass vials with teflon-lined caps for volatiles; glass jars with foil-lined caps for solvent extractables; and glass jars for density estimates. All samples were kept refrigerated in the dark until submitted for analyses.

## (iii) Sample Analyses

Generally, all samples were analyzed for selected major elements (Al, Fe, Mg, Mn) and metals (Cd, Co, Cr, Cu, Hg, Ni, Zn, Pb), chlorinated hydrocarbons (PCB's, p',p'-DDT, p',p'-DDD, o',p'-DDT, Mirex, oxychlordane, hexachlorobenzene, hexachlorobutadiene, hexachloroethane, octachlorostyrene, pentachlorobenzene, tetrachlorobenzene) and for 51 volatile organic compounds. In addition, the concentration of organic carbon, solvent extractables, loss on ignition, total N and P, and particle size distribution were determined in all sediment samples.

All analyses were carried out according to standard MOE methods.

## (c) Results

### (i) Surficial Sediments

The near concentrations of major and trace elements in surficial sediments collected at the sampling stations within 100m of the Canadian shore of the St. Clair River are shown in Figures 4.3.2 to 4.3.7. The concentrations in all Figures represent the average of results obtained from duplicate samples collected at each sampling station. Detailed analytical results are presented in Appendix 4.4.



ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

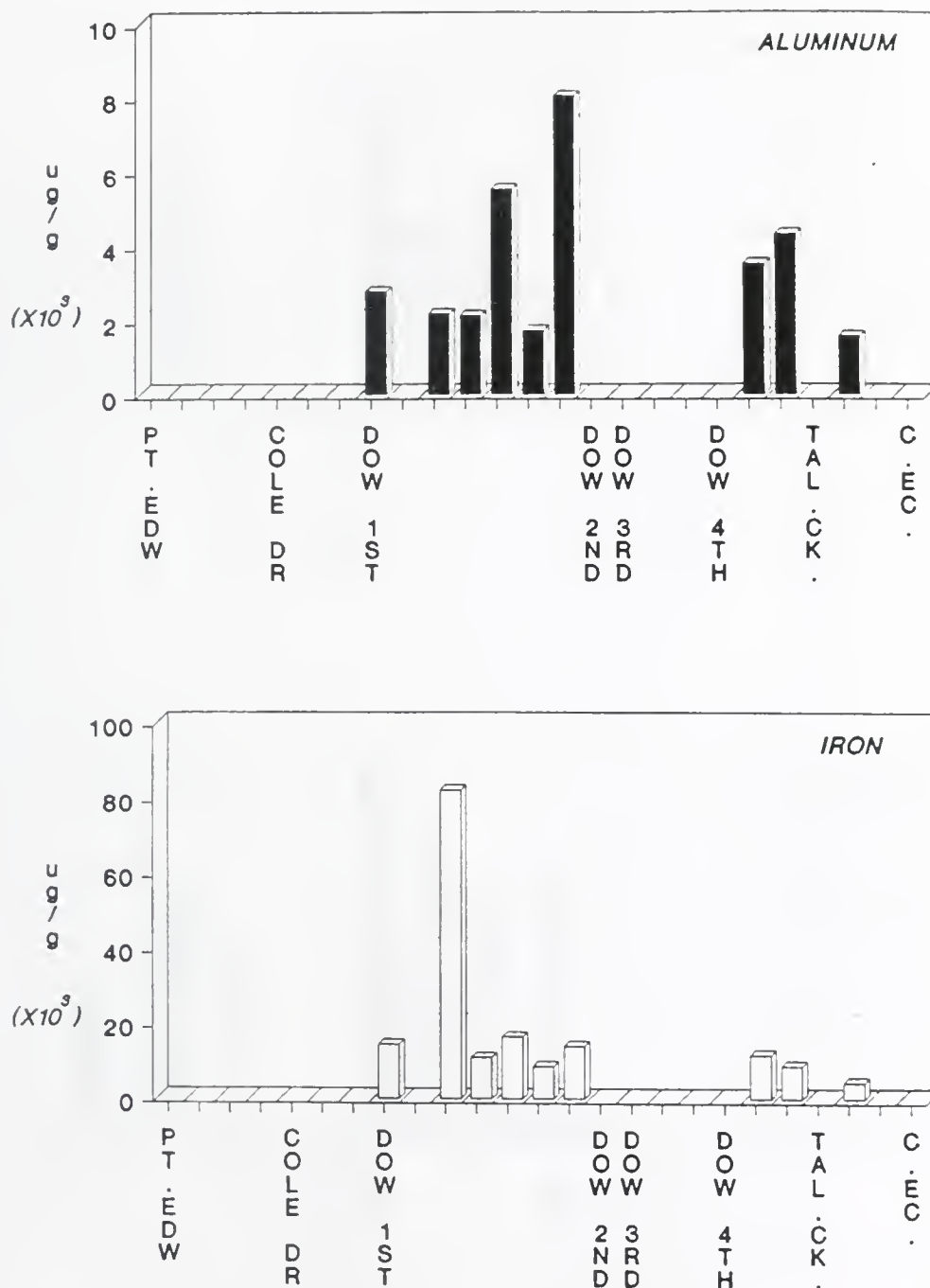


FIGURE 4.3.2: Al and Fe concentrations in sediments from the St. Clair River

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

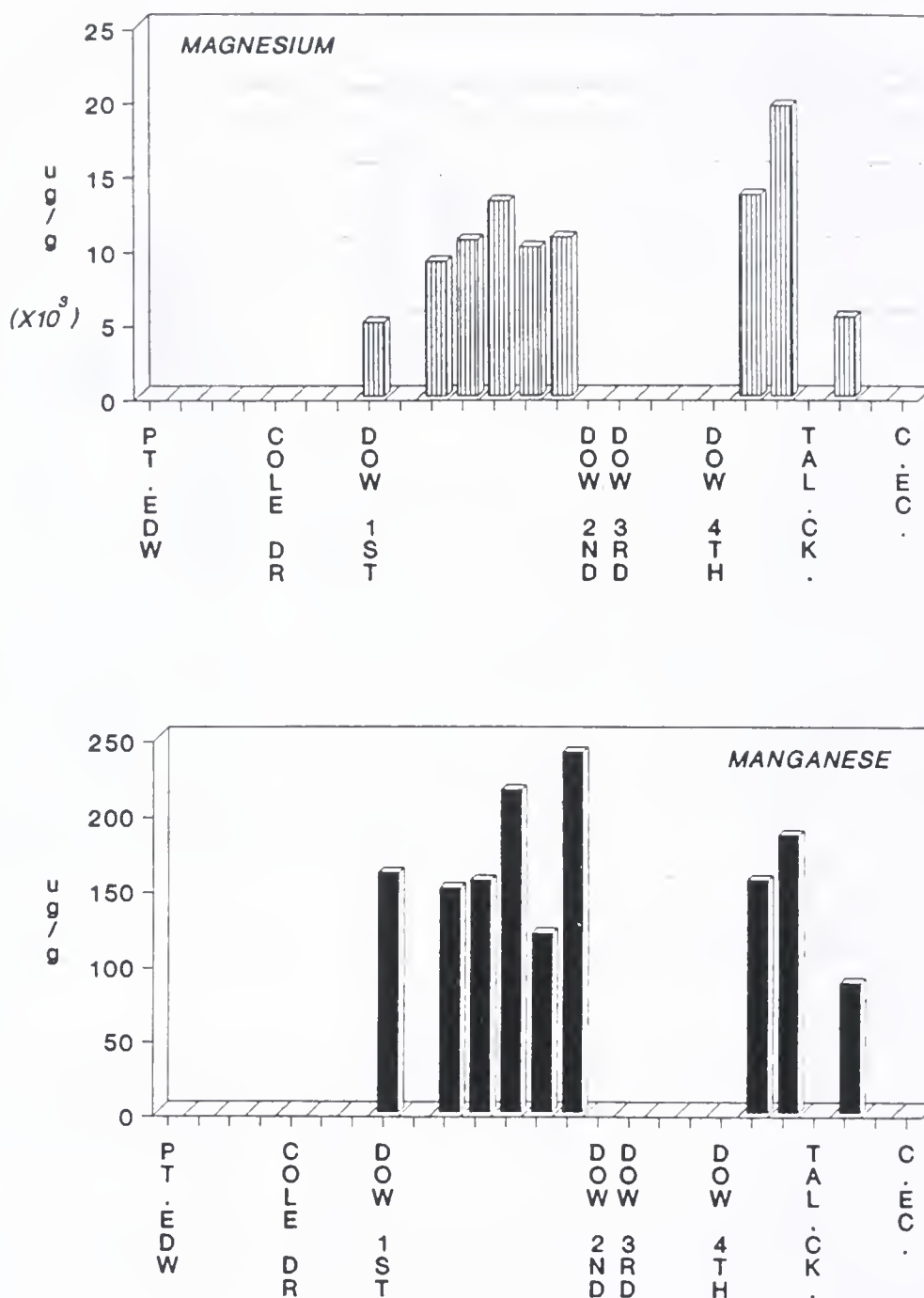


FIGURE 4.3.3 Mg and Mn concentrations in sediments from the St. Clair River

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

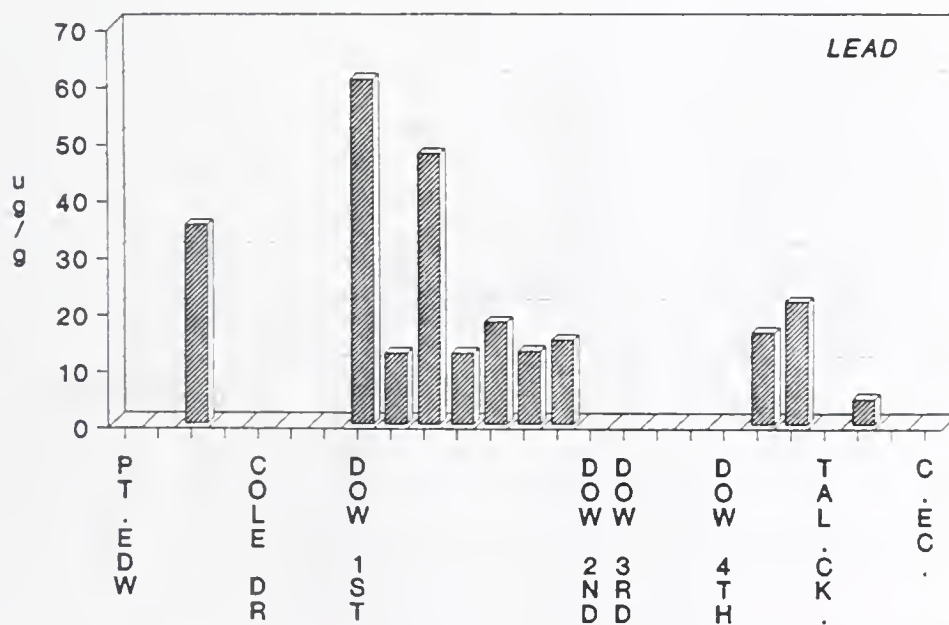
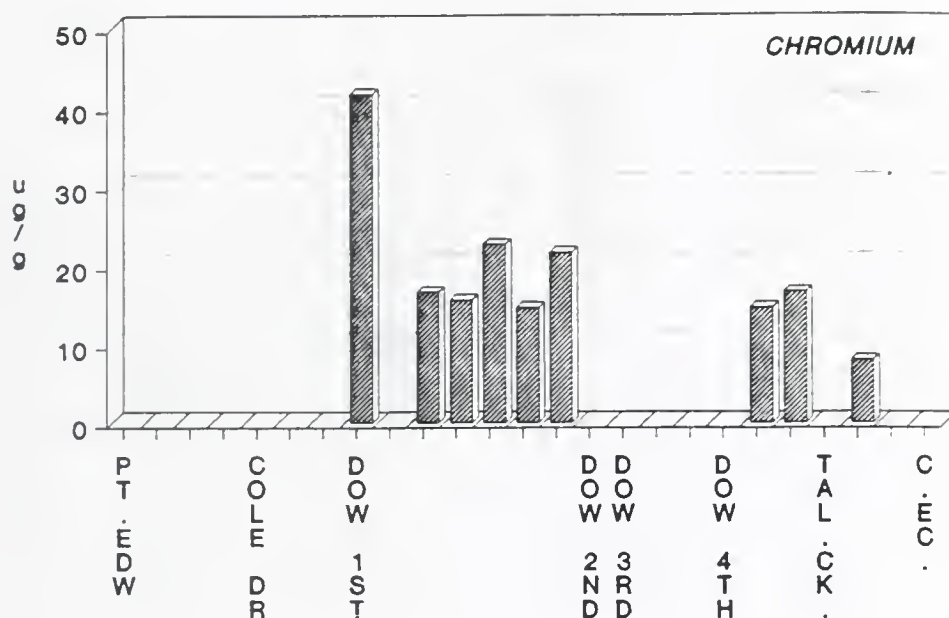


FIGURE 4.3.4 Cr and Pb concentration in the sediments from the St. Clair River

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

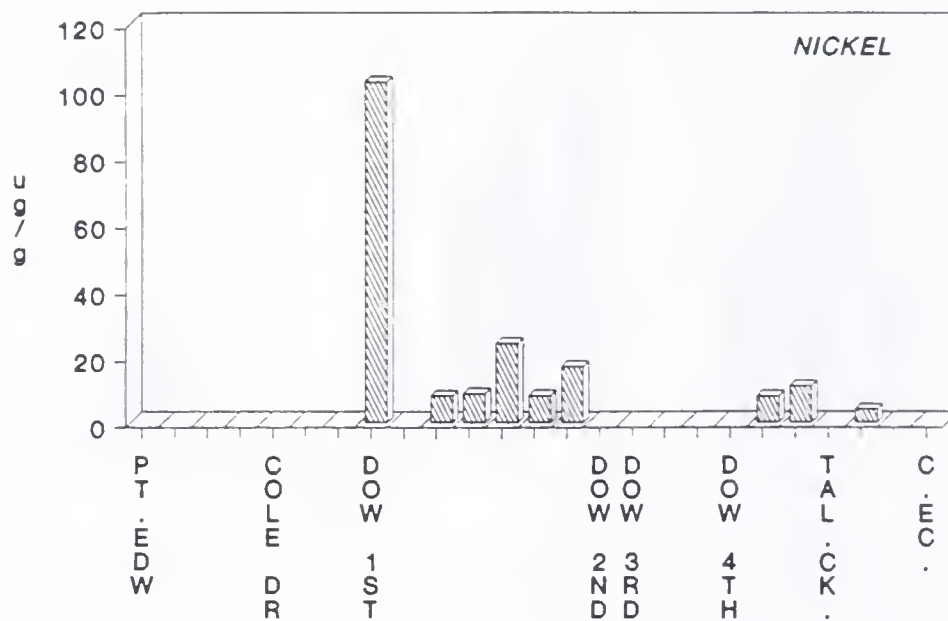
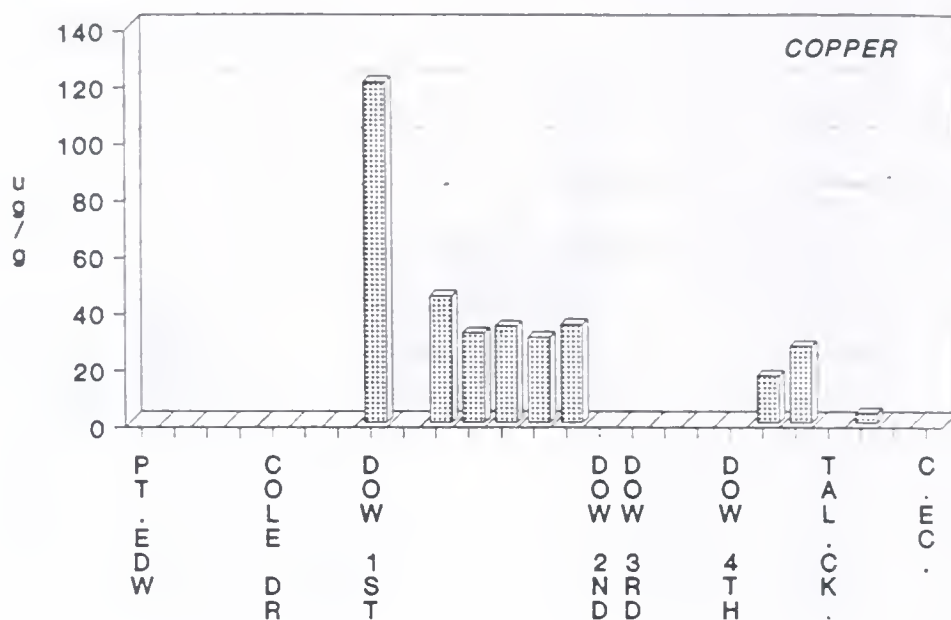


FIGURE 4.3.5 Cu and Ni concentrations in sediments from the St. Clair River

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

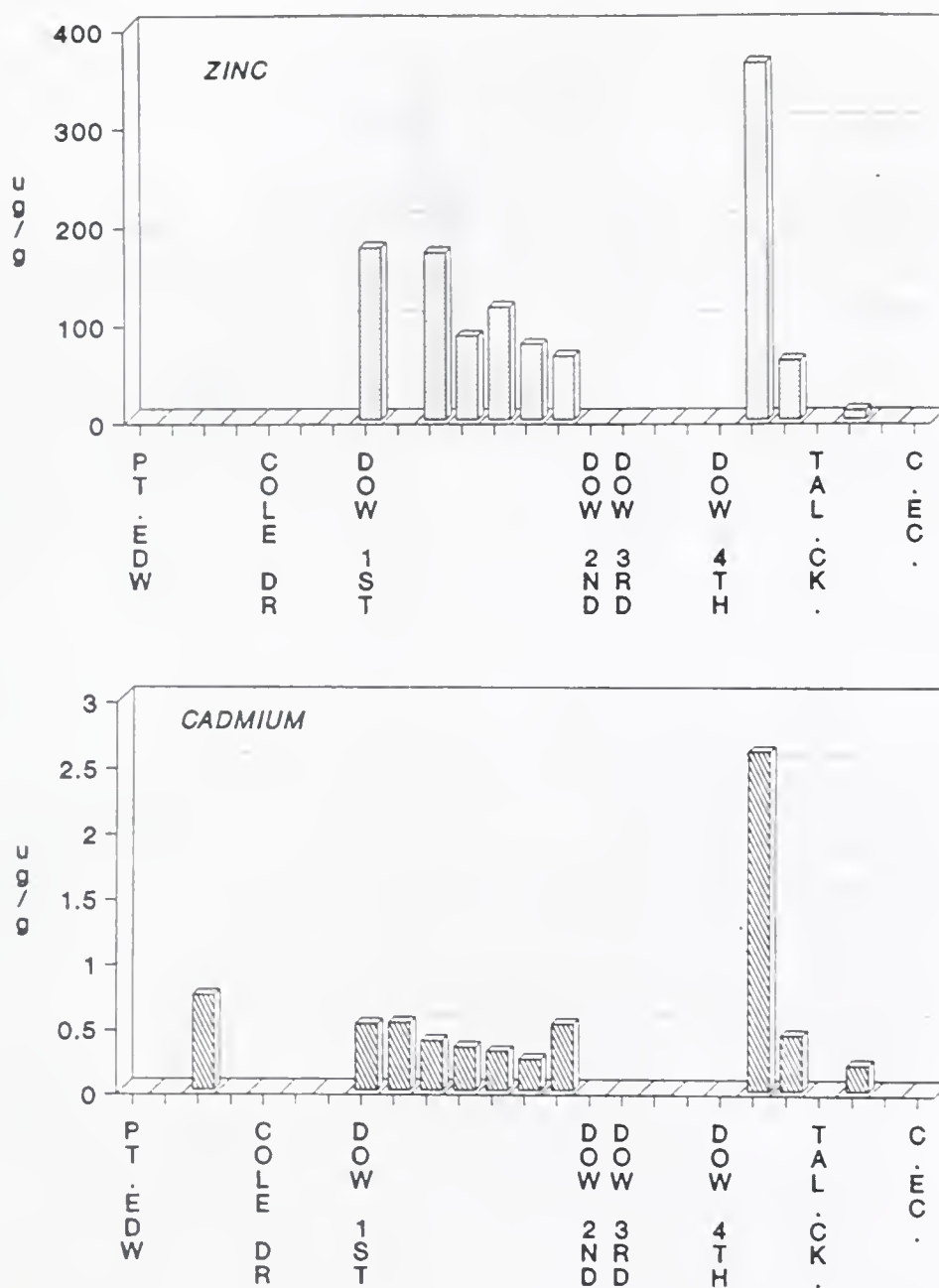


FIGURE 4.3.6 Zn and Cd concentrations in the sediments from the St. Clair River

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

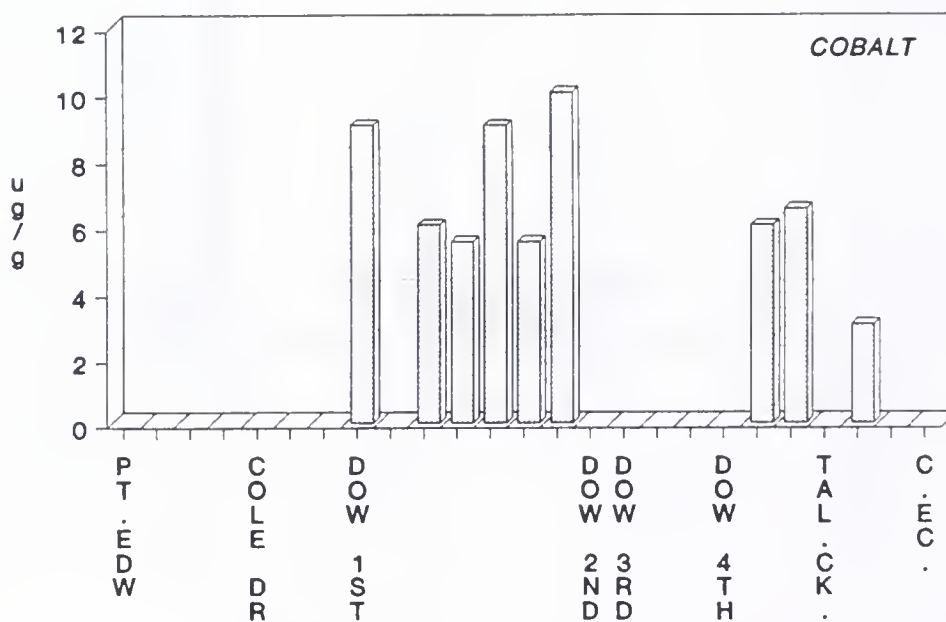
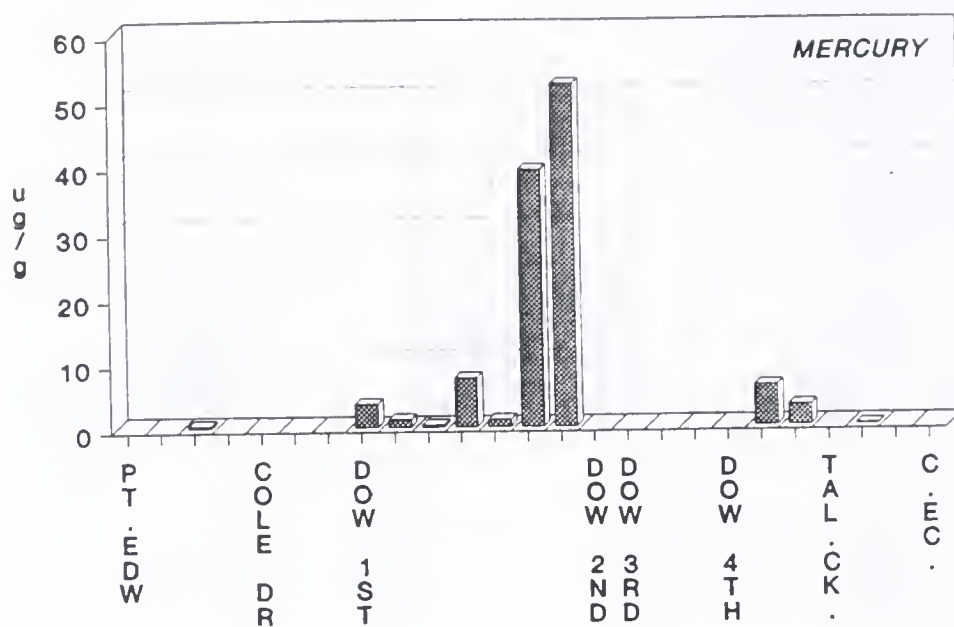


FIGURE 4.3.7 Hg and Co concentrations in sediments from the St. Clair River

### Heavy Metals:

Aluminum, Fe, Mg and Mn (Figures 4.3.2 and 4.3.3) are major geochemical elements of soils and bedrock in the Great Lakes (see Section 2.1). They are already present in large concentrations in bottom sediments. Unless there is an intensive point source discharge of these elements into the river, the concentrations of these elements will be more indicative of the sediment geochemistry than a pollution source.

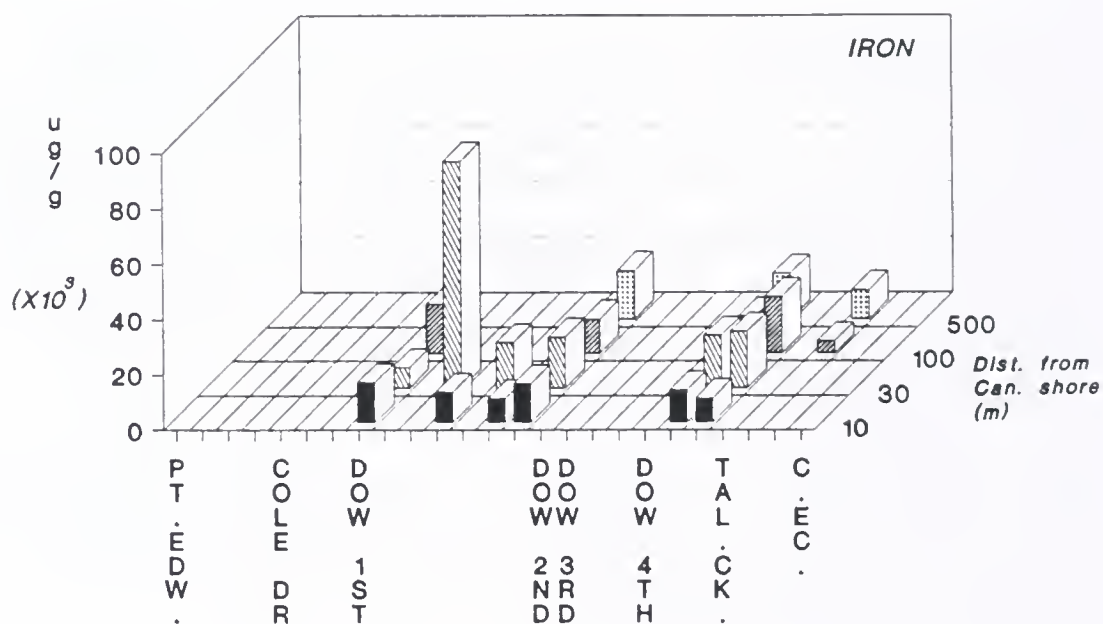
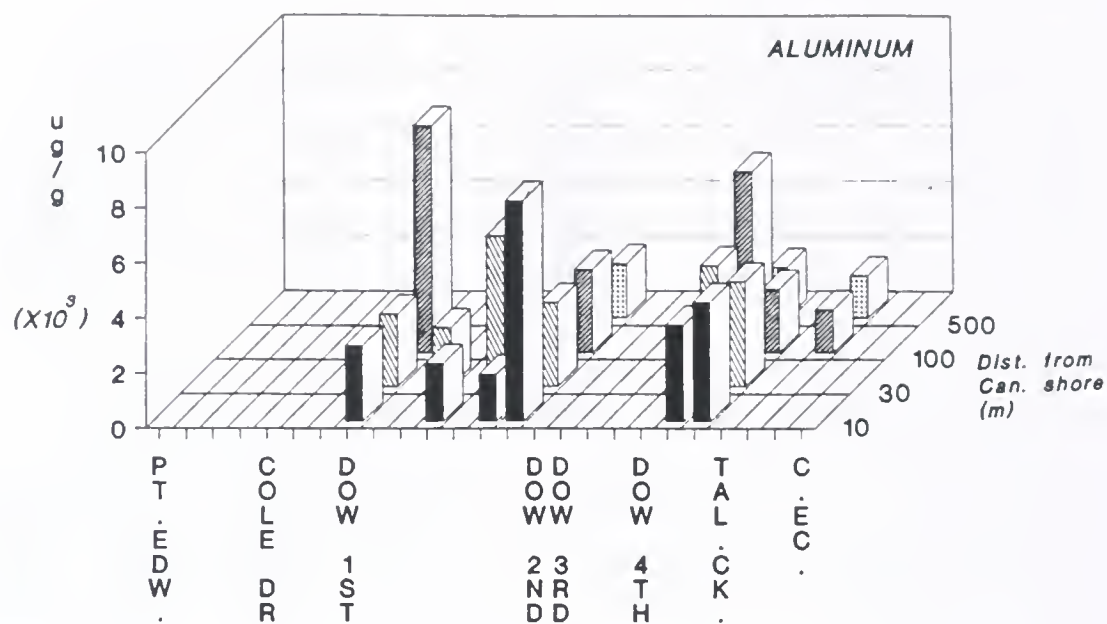
Elevated levels of aluminum (Al) in the sediments is usually indicative of an increase in clay minerals associated with small sediment particles. The greatest concentration of Al in the sediments collected near the shore of the St. Clair River in 1986 was at station 201. The sediments at this station consisted of 34% to 55% of small particles (<45 um). Consequently, the increase of Al in the sediments likely resulted from the increase of clay minerals content.

A substantial increase in iron (Fe) was observed in the sediment samples collected from station 205, about 150m downstream from the 1st Street sewers. Industrial sewage treatment plant effluents could be responsible for this increase. The concentrations of Mg were similar in all sediments collected around the Dow 1st Street complex. The increase of Mg in the sediments downstream from Dow may represent the accumulation of natural material such as dolomite or some clays containing greater concentrations of this element.

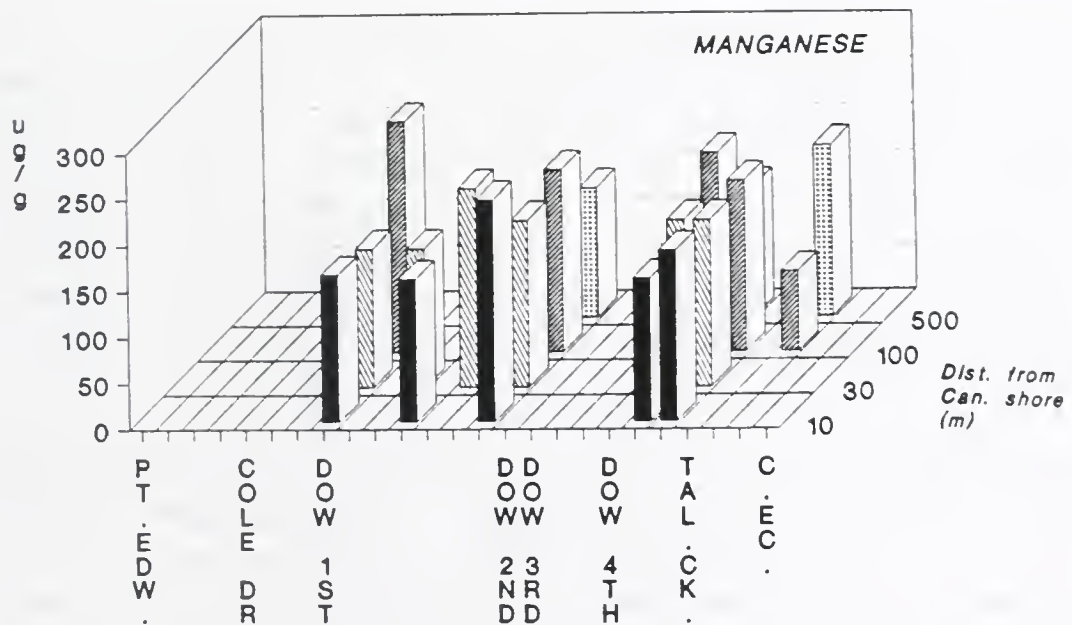
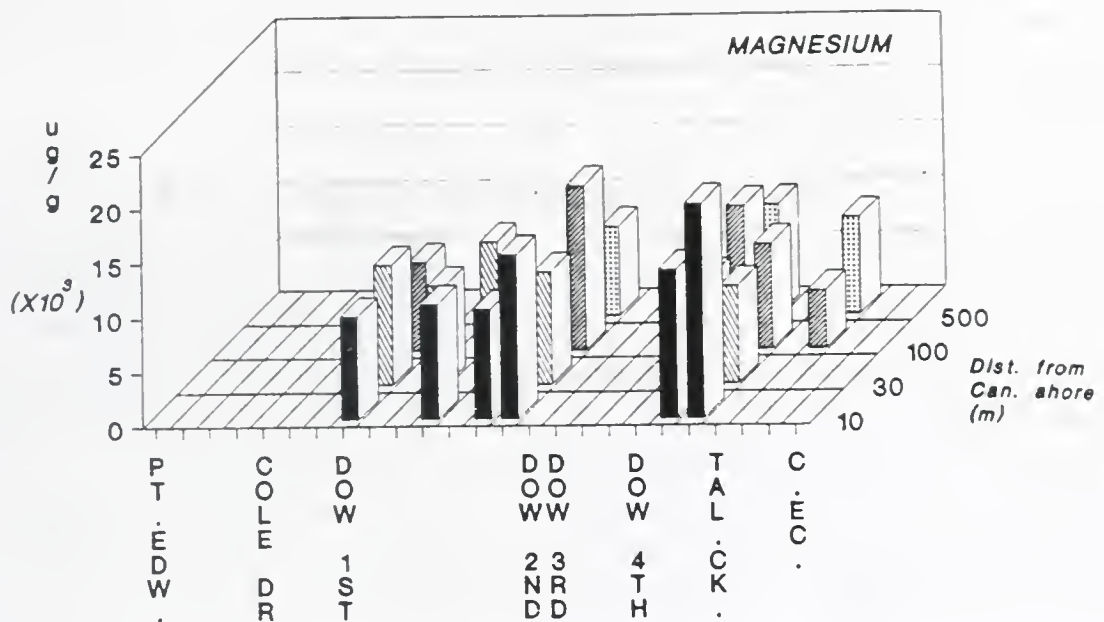
The concentration of Al, Fe, Mg and Mn in sediments sampled across the St. Clair River also indicated that these elements represent more the geochemistry of the river sediments than input from local sources (Figures 4.3.8 and 4.3.9).

The concentrations of Cr, Cu, Ni and Pb were greatest in the sediments collected at Dow's 1st Street (Figures 4.3.4 to 4.3.5),





**FIGURE 4.3.8** Al and Fe concentrations in sediments collected along a transect across the St. Clair river



**FIGURE 4.3.9** Mg and Mn concentrations in sediments collected along a transect across the St. Clair River

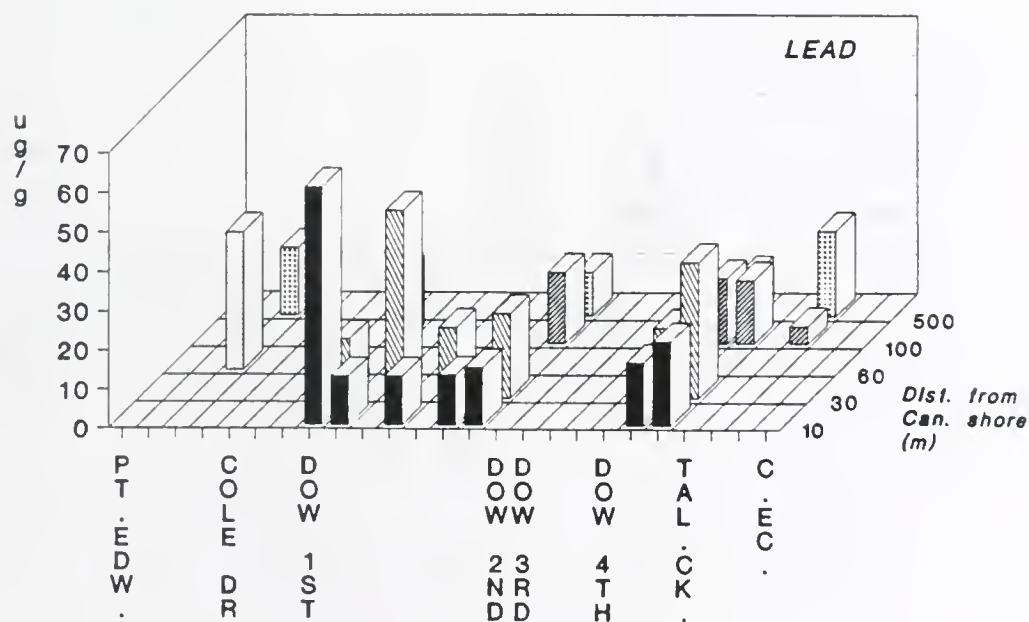
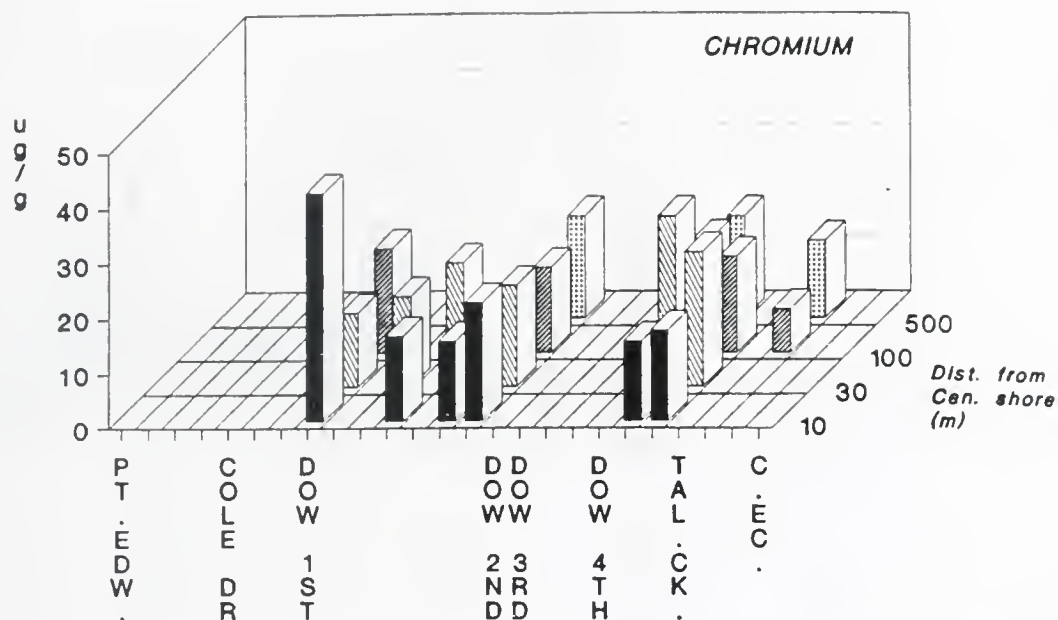
and decreased with increasing distance from the Canadian shore (Figures 4.3.10 and 4.3.11) indicating a likely source at Dow's 1st Street. The largest concentration of Cd and Zn occurred in the sediments downstream of the Dow 4th St. sewer at station 216 near the Canadian shore (Figures 4.3.6 and 4.3.12).

Concentrations of Hg were extremely high in the sediments at stations 208 (about 400m downstream of Dow's 1st Street sewer) and the next sampling station (no. 201) of the 2nd Street sewer (Figures 4.3.7 and 4.3.13). Mercury was used in the manufacture of chlorine until the early 70's by the Dow Chemical Company. Consequently, it is the element characteristic of their wastes; particularly, in concentrations found at stations 208 and 201. These may also reflect current continuous inputs (Section 4.1.1). The concentrations of cobalt (Co) were similar in all sediment samples (Figures 4.3.7 and 4.3.13), and at the background levels of the Great Lakes sediments.

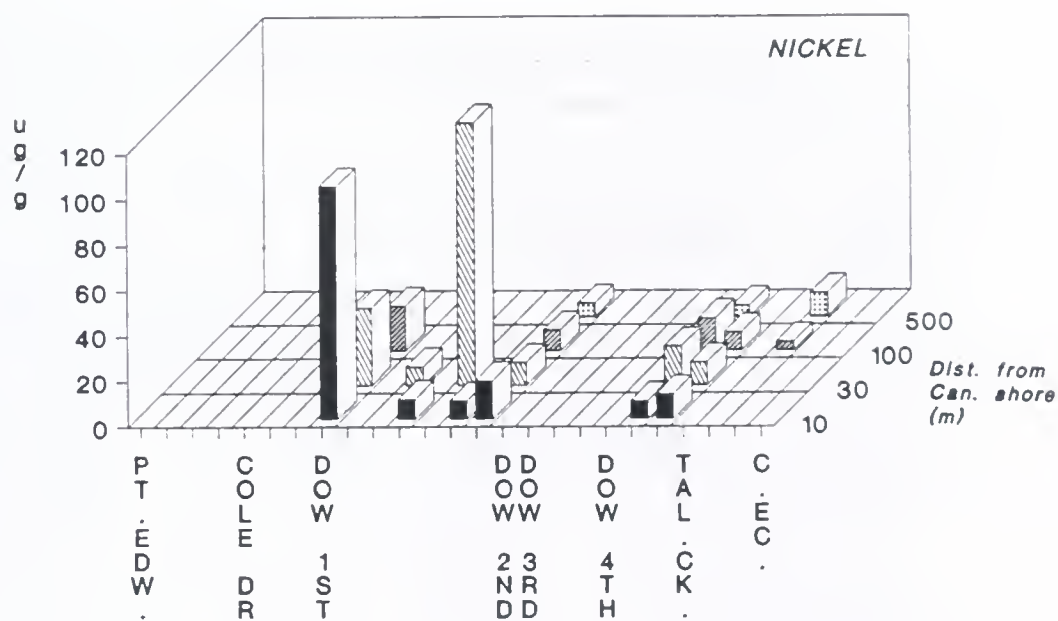
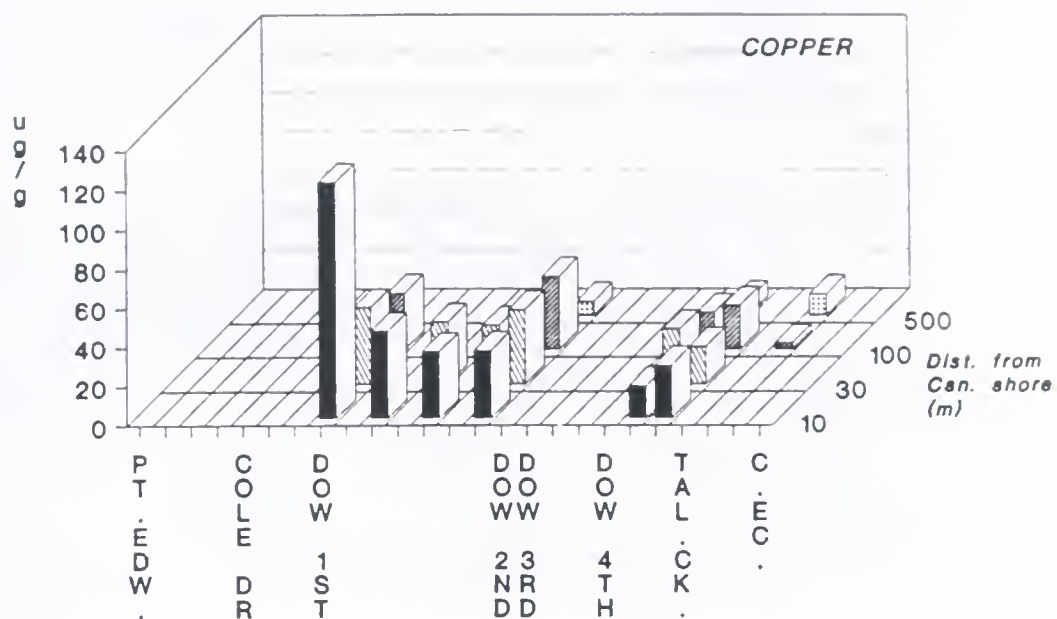
#### Chlorinated Organic Compounds:

Hexachlorobenzene, hexachlorobutadiene, hexachloroethane, octachlorostyrene, and tri-,tetra- and pentachlorobenzene were found in large concentrations in the sediments collected within 100m of shore at stations located between Dow's 1st and 2nd Streets sewers (Figures 4.3.14 to 4.3.18). As shown in previous studies, these contaminants originate from sources at Dow (Oliver and Pugsley 1986; DOE/MOE 1986). The greatest concentrations of PCB's were found in the sediments collected about 150m downstream from Dow's 1st Street complex.

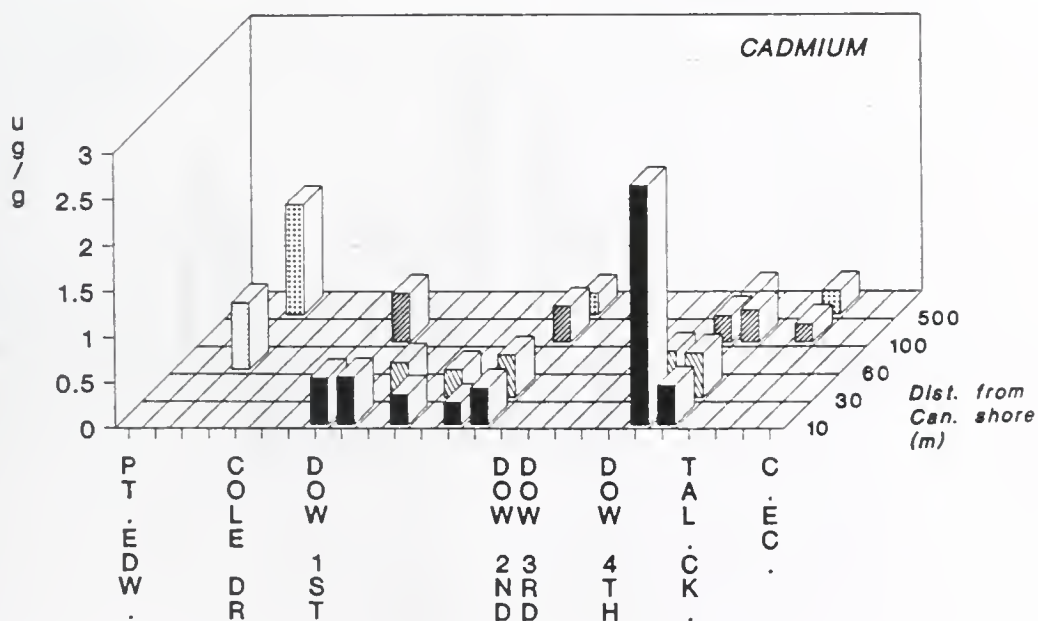
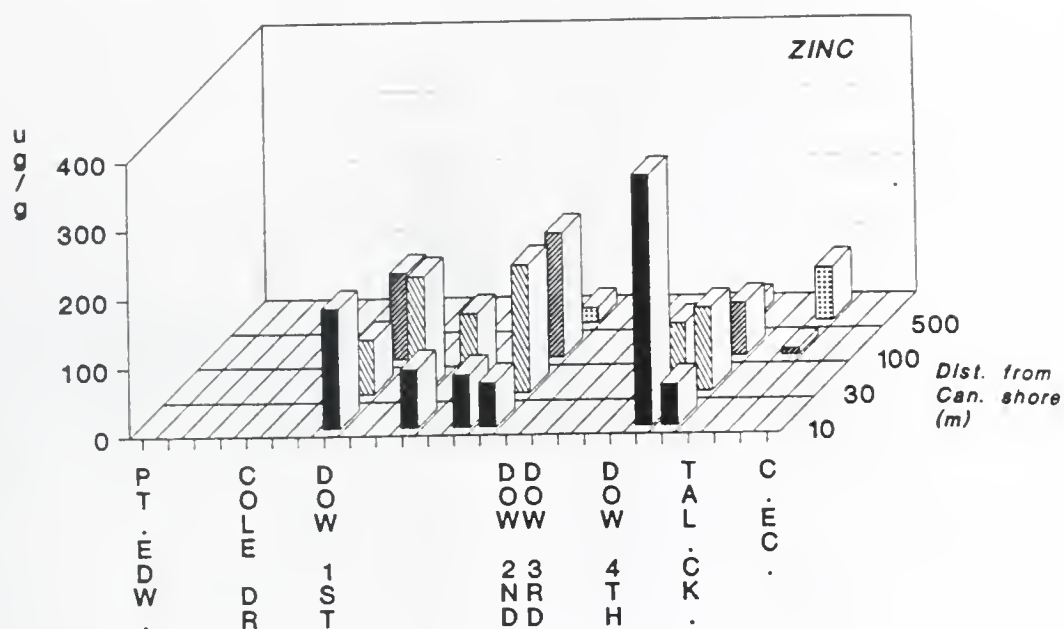
The concentrations of all organic contaminants analyzed were generally below the detection limit for sediments collected upstream from Dow (station 202). Concentrations of contaminants decreased in the sediments collected downstream of the 2nd Street sewer outfall, and towards the western shore of the St. Clair River to near the detection limit. The concentrations of contaminants in sampled sediments indicated a point source discharge at Dow's 1st and 2nd Street sewer outfalls.



**FIGURE 4.3.10** Cr and Pb concentrations in sediments collected along a transect across the St. Clair River



**FIGURE 4.3.11** *Cu and Ni concentrations in sediments collected along a transect across the St. Clair River*



**FIGURE 4.3.12** Zn and Cd concentrations in sediments collected along a transect across the St. Clair River



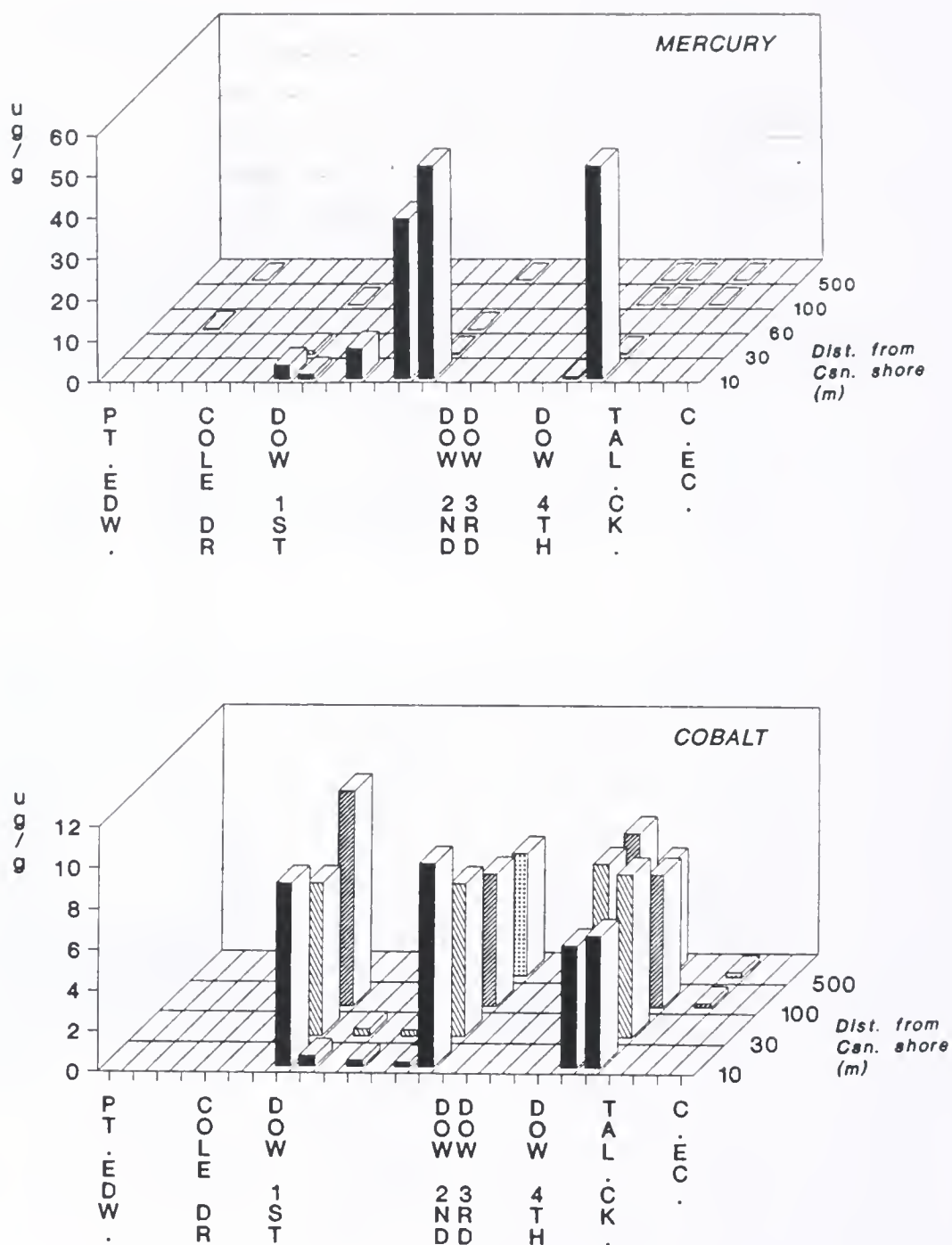


FIGURE 4.3.13 Hg and Co concentrations in sediments collected along a transect across the St. Clair River



ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

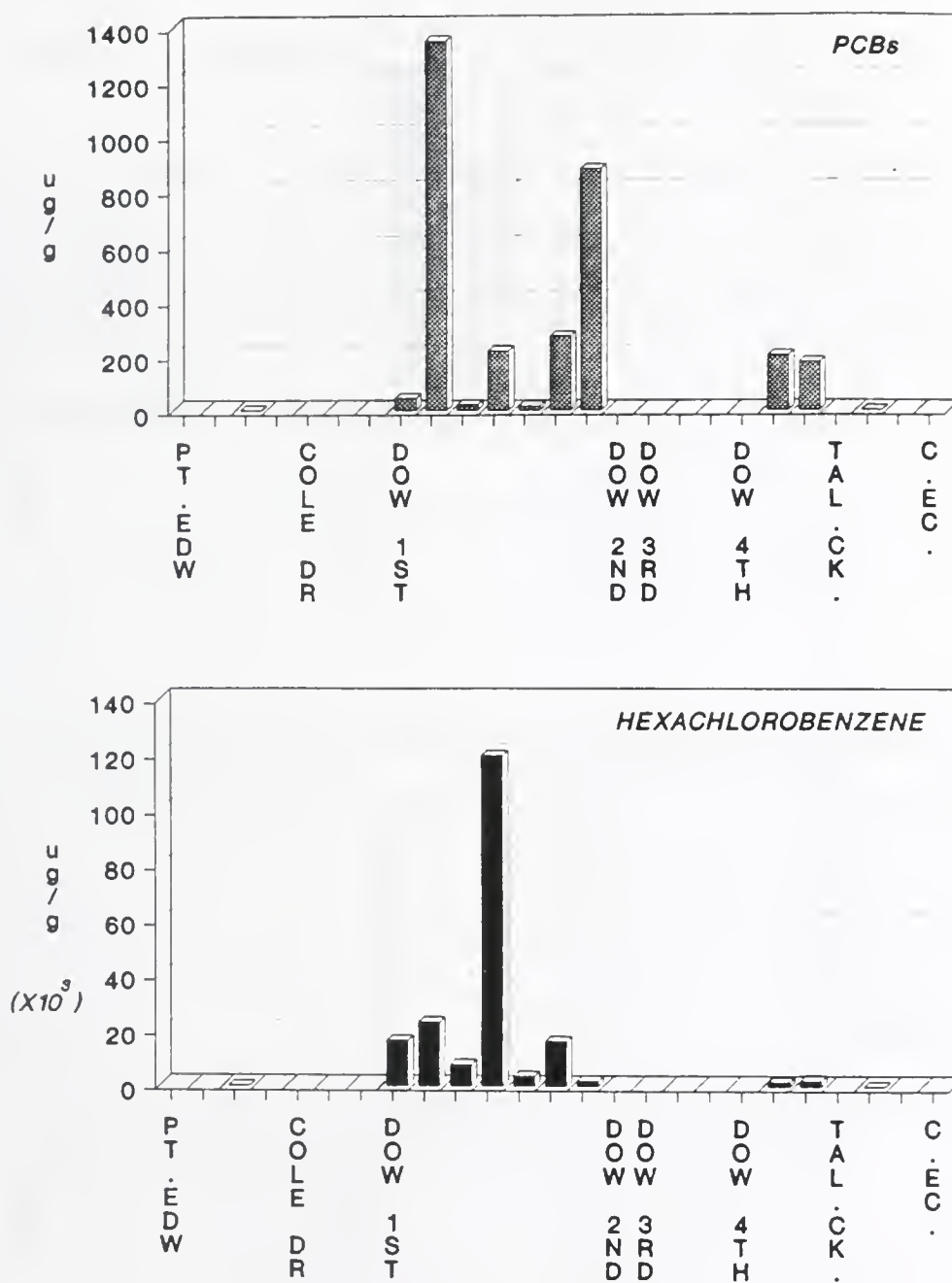


FIGURE 4.3.14 PCB's and hexachlorobenzene concentrations in St. Clair River sediments

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

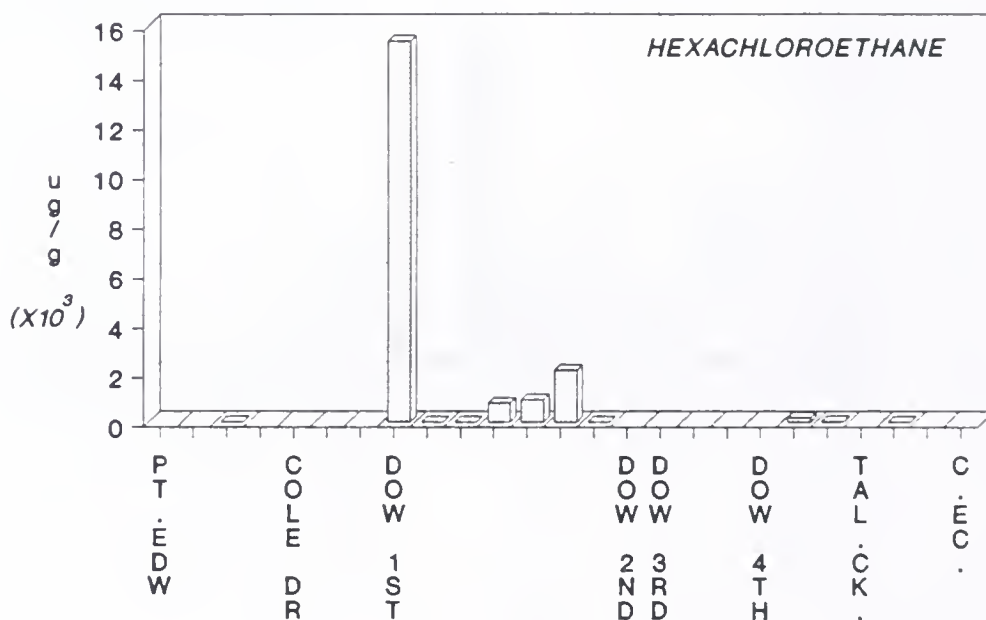
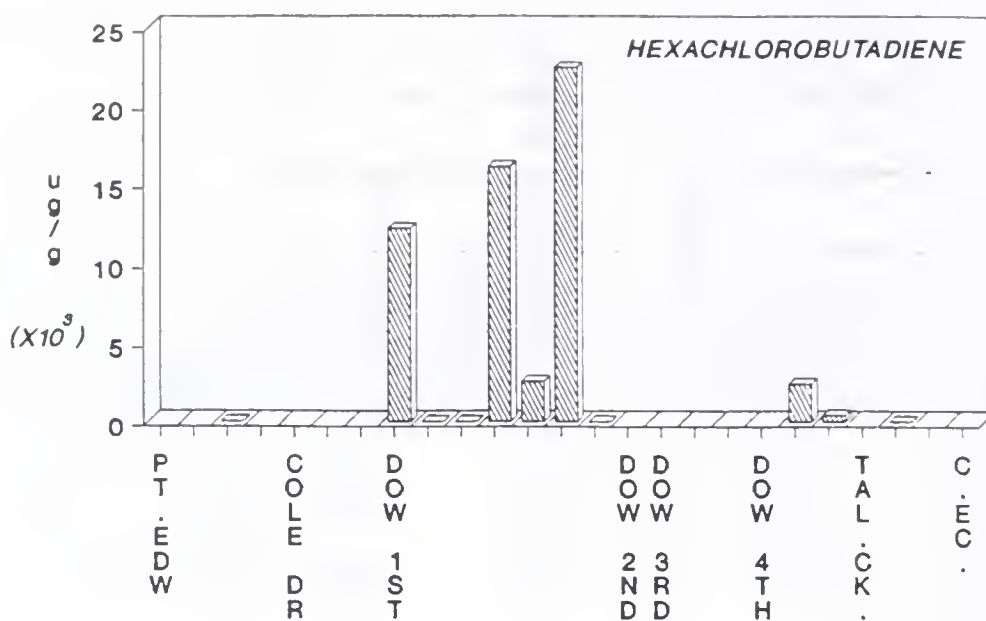


Figure 4.3.15 Hexachlorobutadiene and hexachloroethane concentrations in St. Clair River sediments

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

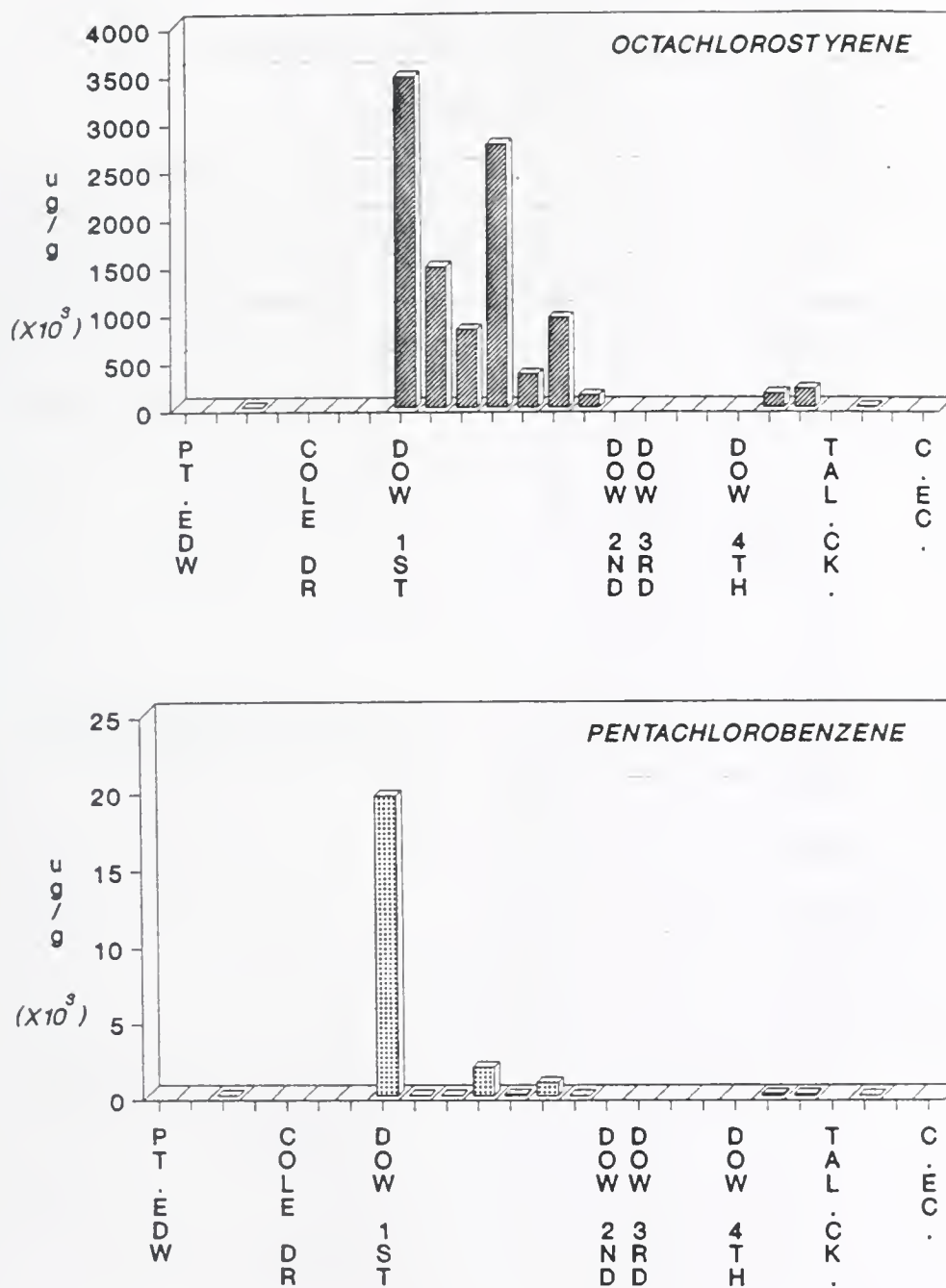


FIGURE 4.3.16 Octachlorostyrene and pentachlorobenzene concentrations in St. Clair River sediments

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

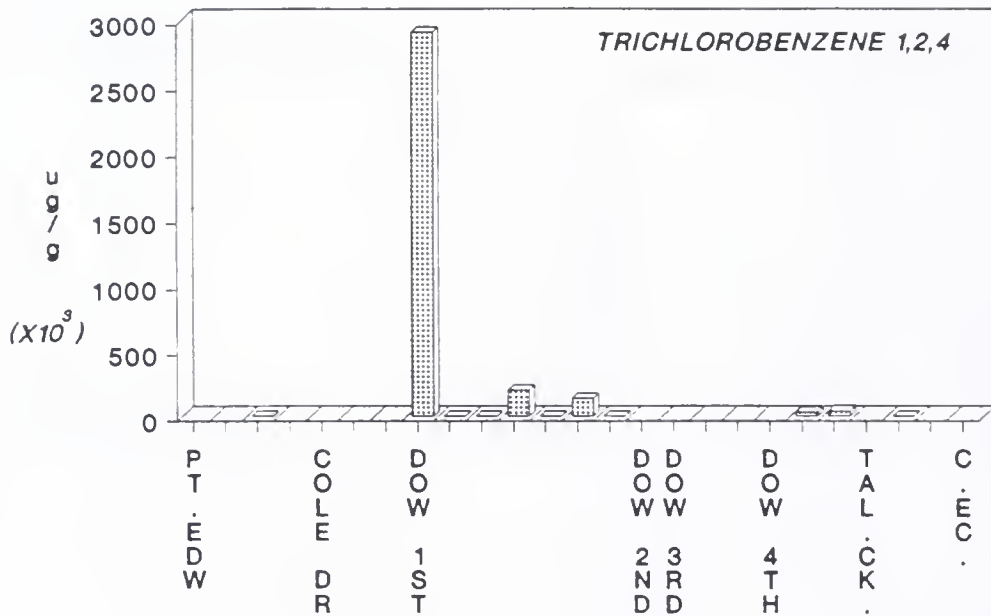
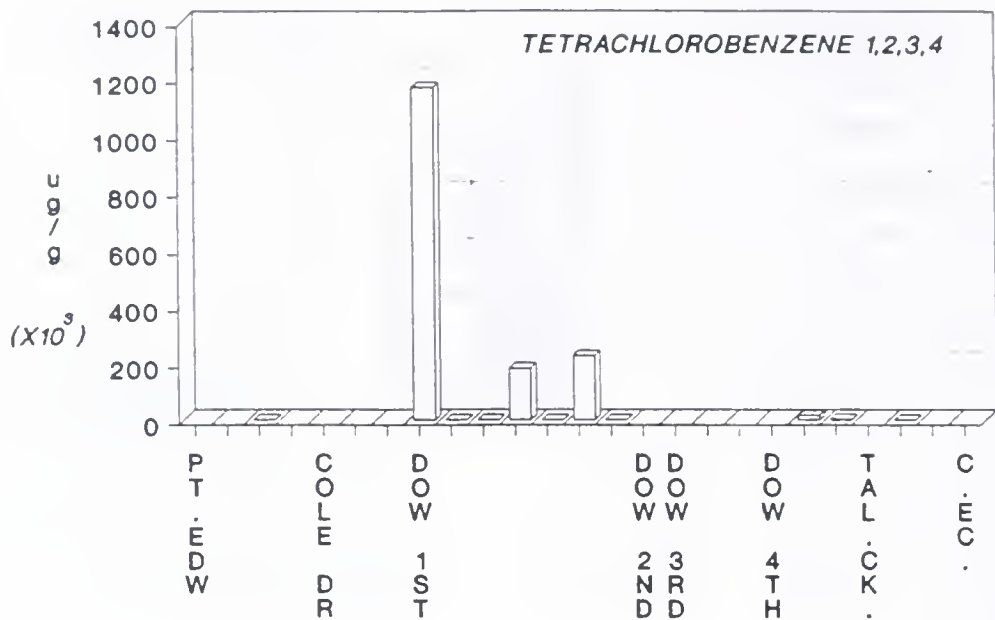


FIGURE 4.3.17 Tri-and tetrachlorobenzene concentrations in St. Clair River sediments

ST. CLAIR RIVER SURFICIAL SEDIMENT RESULTS - 1986

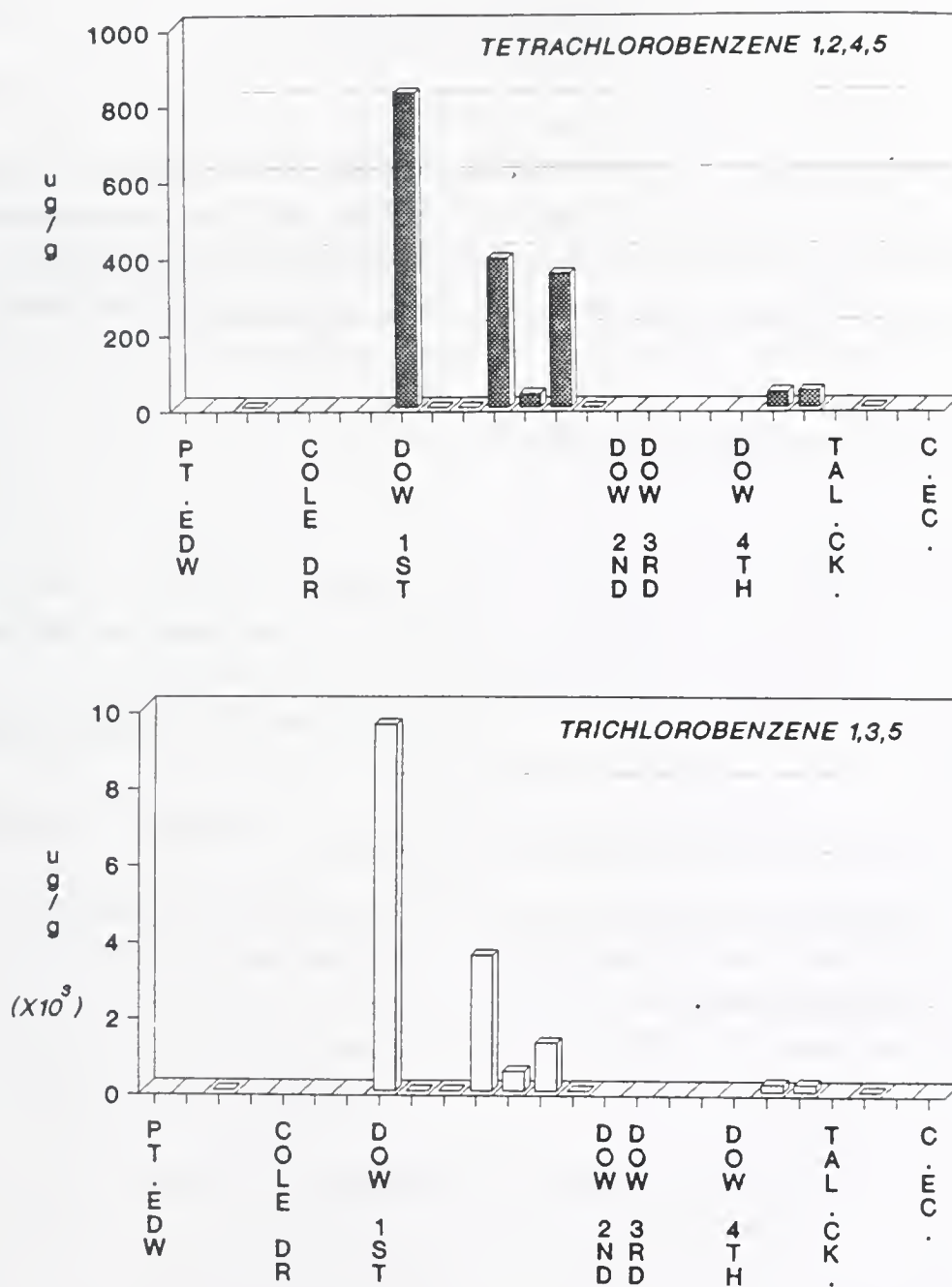


FIGURE 4.3.18 TRI-AND TETRACHLOROBENZENE IN ST. CLAIR RIVER SEDIMENTS

(d) Discussion

(i) Comparison of data with existing guidelines/criteria

Sediment samples exhibited elevated levels of total organic carbon (TOC), which exceeded the recommended MOE Open-Water Disposal Guideline of 10 mg/g. The heavy metals copper, mercury and zinc were elevated in the sediments at Station 203 in the Chemical Valley and at several other stations downstream (MOE Guideline: Cu - 25 µg/g, Zn - 100 µg/g, Hg - 0.3 µg/g).

Benthic Invertebrates and Sculpins

In October 1986, nine stations in the St. Clair River were surveyed by the Aquatic Biology Section of the Water Resources Branch as part of the In-Place Pollutants Program. The stations were selected on the Canadian side of the river between Sarnia Bay and the Chenal Ecarte/South Channel. The study investigated several components associated with the sediments, these were:

- 1) Surficial sediment chemistry: (≈top 5 cm)
- 2) Bottom water chemistry: 1 meter off the sediment surface
- 3) Contaminant levels in benthic invertebrates, e.g.:
  - a) mayfly nymphs
  - b) amphipods
  - c) chironomids
  - d) leeches and
  - e) bottom-feeding fish (e.g. sculpins), and
- 4) Benthic community structure.

Benthic Community Structure at each of the stations where benthic invertebrates were present suggested no adverse effect. These results were supported by a similar study conducted in 1985 and reported in Section 4.4.6. The stations that were sampled had either fine or

coarse sediment. This was determined largely by the station being in either a depositional zone or in an open stretch of the river. The In-Place Pollutants Program attempted to focus their study on depositional zones.

Results of the 1986 In-place Pollutants study indicated that benthic invertebrates and sculpins had bioaccumulated all analyzed metals (Cu, Cr, Zn, Cd, Hg, Ni) as well as the organic contaminants HCB, HCBD, naphthalene and perylene. It was also observed that metal levels in sculpin tissues were higher relative to levels in benthic invertebrates. Sculpins bioaccumulated octachlorostyrene (OCS) and DDE in their tissue. Benthic invertebrates had detectable levels of DDD in their tissue.

HCB and OCS levels in Hexagenia were positively correlated with sediment contaminant levels (section 4.4.7).

#### (ii) Comparison with Historical Data

##### Temporal Trends based on Sediment Bioassay Studies

It has been demonstrated that severe impairment of the benthic community for the entire length of the river existed in 1968; and for about 20 km downstream of Sarnia in 1977. Findings from a 1985 study (Section 4.4.6) of the benthic community indicates a much reduced zone of impairment (Griffiths 1988).

Bioassays conducted in 1985, shortly after a spill of tetrachloroethylene and follow up studies several months later found that the sediments in the vicinity of Dow and Polysar were acutely toxic to test organisms. The results of the present study (Section 4.3.2) indicate that conditions in 1986 were similar to non-spill conditions in 1985.



### (iii) Sediment Transport - Contaminant Monitoring

In order to obtain a better understanding of the contribution of various sources of contaminants to the bottom sediments, it is important to quantify the flux associated with Suspended Solids. Samples for this purpose were collected in 1984 (Johnson and Kauss 1987) and again as part of the MISA investigation (Section 4.2.1). Water was pumped from mid-depth and centrifuged in order to obtain a minimum of 25 grams (wet weight) of solids. The suspended sediment samples were analyzed for PCBs, chlorinated aromatics [hexachlorobenzene (HCB), octachlorostyrene (OCS)], and heavy metals [iron (Fe), mercury (Hg), lead (Pb), zinc (Zn)]. These centrifuged particulates were also analyzed for solvent extractables and total organic carbon (TOC).

Results of 1984 findings were consistent with values obtained during the MOE intensive investigation carried out in 1986. Detailed findings of this latter study are presented in Section 4.2.1.

### Sediment Transport - Sedimentation

There is very little sediment accumulation in the river. Essentially only a coating of sand and gravel has established itself over the glacial clay (Oliver 1988). There are occasional pockets of deeper sand, probably due to filling of inundations in the glacial till.

Radionuclide age measurements from a deeper sand core collected near Sarnia indicated the following:

- the 0 to 3 cm interval: less than nine months old,
- the 3 to 8 and 8 to 13 cm interval: from one to ten years old, and
- the 13 to 18 and 18 to 24 cm interval: from ten to thirty years old.

Thus, over most of the river, where thin unconsolidated sediments are found, the sediments are dynamic and transitory with a river retention time of less than one year. In bands of deeper sand strata, bottom layers of this material may be retained for many years (Oliver 1988).

#### Bedload Transport and its Significance to Contaminant Movement

Bedload transport was measured in May, 1986 at three locations along the St. Clair R. (Oliver 1988). Transects consisted of 10 stations segregated by approx. 50-70 m perpendicular to river flow at Imperial Oil (Sarnia), directly below Dow Chemical (Sarnia) and at Port Lambton. Samples were collected using an Arnhem basket sampler.

Measurements indicated that the quantity of bedload transported in the river was very small. Concurrent measurements of suspended sediment load, demonstrated it to be 3 orders-of-magnitude greater than the bedload transport. Bedload transport accounted for less than 0.5% of the total contaminant loading.

#### (iv) Discussion of Technique Assessment

There were 23 sediment sampling stations selected for this MISA investigative survey. However, there was only one station located upstream of the point sources. The selection of sampling sites in this survey was affected by many recent studies showing the location of the contaminants source in the St. Clair River. Without this detailed knowledge gathered through recent studies, the 23 sediment sampling stations selected for this survey would not have been sufficient to pinpoint contaminant sources in the complex St. Clair riverine system, with its highly industrialized areas. In a highly dynamic system, such as the St. Clair River sediments, physico-chemical properties and concentrations of contaminants may change considerably within a 1 m<sup>2</sup> area of the river.

The results of the present survey, particularly the particle size distribution, indicated heterogeneous sediments with different properties over a small area in the river.

The data set relevant to particle size distribution for collected sediment samples is extensive. A determination of the quantity of <45  $\mu\text{m}$  particles, >63  $\mu\text{m}$  particles, and >500  $\mu\text{m}$  particles will give sufficient information on the sediment type.

Some correlation was found between a few parameters in the sediments, mainly between the concentration of organic carbon and particles <45  $\mu\text{m}$ , and organic carbon and PCB's. However, it was difficult to interpret these relations because of the heterogeneity of the sediments and large concentrations of organic contaminants near the point source. More sampling stations would be necessary to interpret the ratios of organic contaminants which may point to specific sources.

The interpretation of an extensive data set, with general information on sampling, like that for the sampling and analyses of the sediments in the St. Clair River, requires expertise in sedimentology, sediment geochemistry and a knowledge of organic contaminants originating from different industrial wastes. It is very important to set clear objectives for the selection of sediment sampling stations.

Generally, the majority of the data should be processed by a computer using various software, such as a statistical package and Lotus 1,2,3, or a similar package for the production of graphics. High concentrations of organic contaminants in the sediments between Dow's 1st and 2nd Streets in the St. Clair River may affect results of other techniques for the assessment of the toxicity of industrial effluent at the site. The bottom sediments have to be considered a sink as well as a source of pollutants. It may be difficult to distinguish the effects (and concentrations) of contaminants in sewer effluents from those released from the sediments, particularly in the far-field

where the influence of point sources relative to the sediments may be far less significant.

(e) Critique of the Assessment Method:

Despite a knowledge of suspected/potential contaminant sources, there should be:

- (1) additional control stations located upstream of the Dow discharges;
- (2) an increase in the number of sampling stations on the transects perpendicular to the direction of river flow;
- (3) more sediment sampling stations downstream of suspected sources, in order to assess the extent of contamination and the transport of sediment-associated contaminants from the point source;
- (4) Duplicate sediment samples from one site should be collected with a double-Shipek grab sampler, so as to assure the closest proximity of a duplicate sample at one station;
- (5) The accurate position of the sampling vessel should be recorded, when using a single grab sampler, so as to estimate the distance between the "duplicate" sampling points.

4.3.2 Sediment Toxicity

(a) Methods

Sediment samples for toxicity testing were collected October 7-14, 1986 (Figure 4.3.19) as part of the MOE In-place pollutants program. Details on the method of collection, sediment description and quality, benthic-invertebrate contaminant levels and benthic-invertebrate

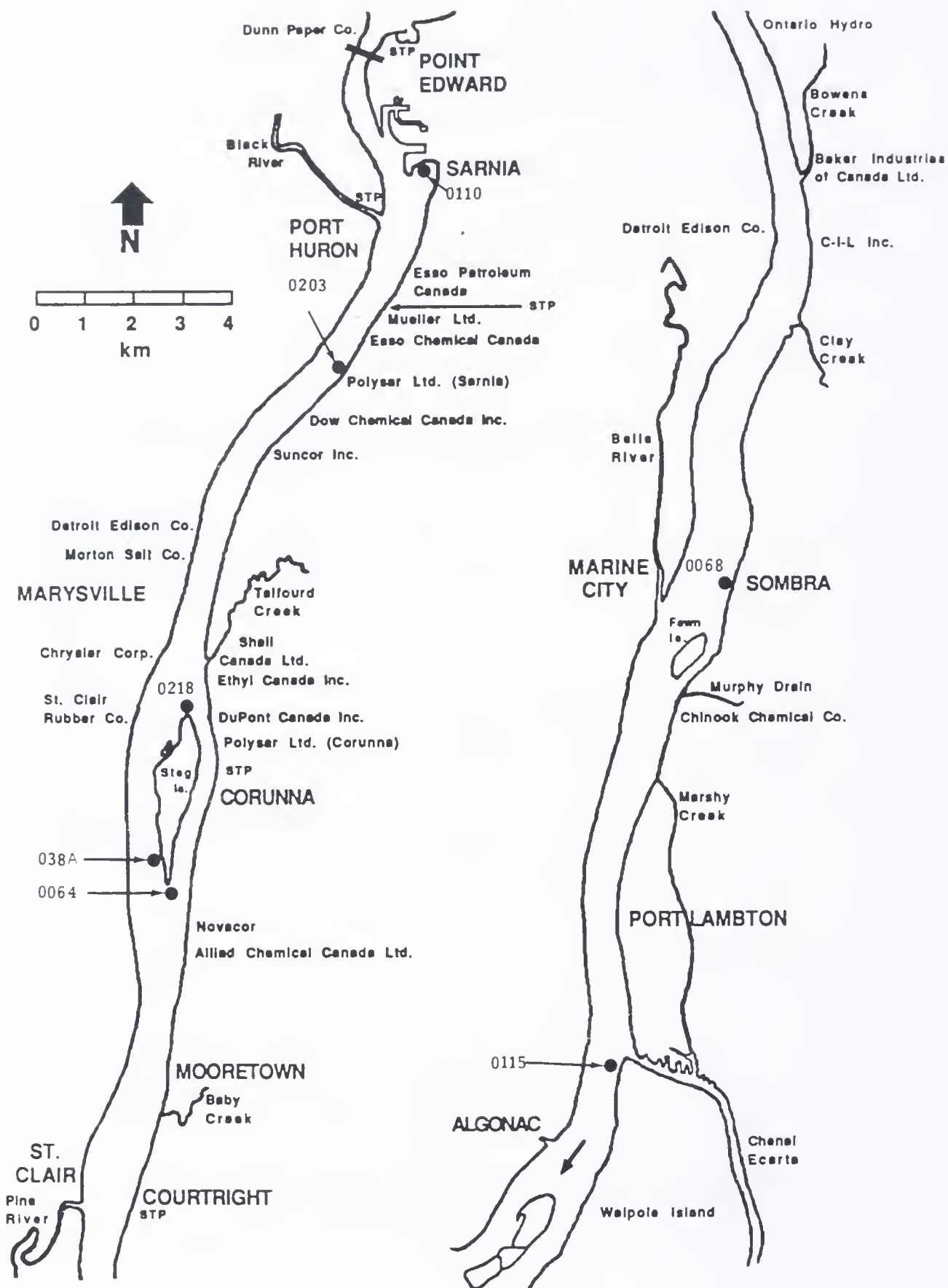


FIGURE 4.3.19 LOCATION OF SEDIMENT BIOASSAY COLLECTION SITES IN THE ST. CLAIR RIVER

community structure are included in section 4.4.6. Sediment samples were shipped to the laboratory in buckets lined with food grade plastic bags, and were stored at 4°C until tested.

Prior to testing, sediments were normally sieved through 3 mm mesh and thoroughly mixed to ensure uniform quality among subsamples. Samples collected in 1985 from the St. Clair River were high in volatile compounds, in particular, tetrachloroethylene. Therefore, as a safety precaution and to minimize losses of volatile compounds that could be toxic to test organisms, these samples were not sieved or mixed.

Bioassays were conducted on fathead minnows (Pimphales promelas) and burrowing mayflies (Hexagenia limbata). The minnows were 4-month-old juveniles cultured in the MOE laboratory from stock obtained from the USEPA Laboratory in Duluth, Minnesota. Mayflies (second-year nymphs) were collected from Georgian Bay in Lake Huron and maintained in the lab for a short period prior to testing. Bioassays were performed in 1.5 L Mason jars. A 200 mL sediment sample was placed in the jar, topped with 800 mL dechlorinated tap water and allowed to settle for 24 hr. The system was then aerated and the test organisms introduced. Tests were conducted separately and in triplicate for each organism, using five minnows or five mayflies per jar. Mortality was recorded daily and dead organisms were removed and discarded.

## (b) Results

Sediment bioassay toxicity results from the seven sampling locations are presented in Table 4.3.1. Survival of the test organisms was 100% in sediments from the control station (0115) which was located upstream of the petrochemical industries. Sediments collected downstream of the Cole drain (station 0203) were acutely toxic to mayflies (14% survival). The sediments were also toxic to minnows but to a lesser extent (67% survival). Sediments were tested from five stations downstream of station 0203. At all of these stations



TABLE 4.3.1: SEDIMENT BIOASSESSMENT RESULTS FROM THE  
ST. CLAIR RIVER

Station	% Survival Fathead Minnow				% Survival Mayfly			
	Rep 1	Rep 2	Rep 3	X	Rep 1	Rep 2	Rep 3	X
0115	100	100	100	100	100	100	100	100
0203	100	0	100	67	20	20	0	13
0218	100	100	100	100	100	100	40	80
038A	100	100	100	100	100	60	80	80
0064	100	100	100	100	100	20	100	73
0068	100	100	100	100	60	100	40	67
0115	100	100	100	100	100	100	100	100



survival of minnows was 100%. Mayfly survival at these stations varied between 67% and 80% except at station 0115, the furthest downstream, where survival was 100%.

(c) Discussion

The sediment bioassay technique used in this study was designed to assess the acute toxicity of the sediments to organisms living in the sediments and in the water column directly above the sediments. Previous studies have shown that when the sediments were found to be acutely lethal to benthic organisms in the bioassay chambers, benthic-invertebrate communities were either absent or severely reduced in the field (Lomas and Krantzberg 1988). Similar data are not available for water column effects; however, in most cases, we would expect conditions in the bioassay chamber to be more severe than in the field.

(i) Spatial Trends

The results of the sediment bioassay indicate that sediments in the St. Clair River above the petrochemical industries were not acutely toxic.

In the vicinity of the petrochemical industries the sediments were acutely toxic to both mayflies and minnows. Field observations made at this site during collection of the sediments revealed that there were few benthic invertebrates present, which supports the findings of this study that the sediments were acutely toxic. It also indicates that the in situ sediments, were having a toxic effect on a wide variety of benthic invertebrate species.

Downstream from the immediate vicinity of the petrochemical industries, survival of minnows was 100% indicating that the sediments were not exerting an acute toxic effect on the water column organisms in the bioassay chamber and therefore would not be expected to exert this toxic effect in the field.

Some mortality of mayflies was found at all but the furthest station downstream indicating that the sediments were having an acute toxic effect on benthic organisms for a considerable distance downstream of the petrochemical industries. The toxicity of the sediments to mayflies did not appear to be correlated with the levels of metals, PCBs, pesticides, chlorophenols, octachlorostyrene or hexachlorobenzene found in the sediments. However, the lowest survival of mayflies was associated with the presence of visible oil (but not solvent extractables) and the highest PAH levels. A study of the St. Marys River by Hiltunen and Schloesser (1983) found that Hexagenia were absent where there was visible oil but present elsewhere. Other studies (Schloesser et al. 1988) in the upper Great Lakes connecting channels found substantially lower densities of Hexagenia in areas with visible oil compared to areas without visible oil.

#### (ii) Temporal Trends

Sediment bioassays conducted on sediments from the St. Clair River in 1985, shortly after a spill of tetrachloroethylene and subsequent follow-up studies several months later found that the sediments in the vicinity of Dow and Polysar were acutely toxic to test organisms as a result of both the spill and general sediment quality conditions. The results of the present study indicate that conditions in 1986 were similar to non-spill conditions in 1985.

### (iii) Contaminants of Concern

The compounds responsible for toxicity found in this study have not been determined. The correlation between visible oil, higher PAHs and lower survival of mayflies, supported by information in the literature (Schloesser et al. 1988) support the hypothesis that PAHs and (or) oils in the sediments are responsible for the toxicity. However, it is unlikely that the levels of PAHs and oils found in the sediments were high enough to cause the mortality of minnows at station 0203.

### (iv) Comparison to Guidelines/Criteria

Policy 5 - Mixing Zones states that no conditions within the mixing zone should be permitted which are rapidly lethal to important aquatic life. Since both mayflies and minnows were killed when exposed to sediments from station 0203, it could be argued that this policy is violated.

## 4.4 Biological Monitoring

### 4.4.1 Heterotrophic Bacteria

#### (a) Introduction

Synthetic organic compounds are commonly introduced into the aquatic environment via effluents from chemical and industrial processes. These organic loadings may result in overburdening of the receiving waters, causing perturbation in the aquatic bacterial community and altering processes which are common to the native microbial populations. Microbial degradation is one of the principle causes for the removal and/or breakdown of organic compounds. Heterotrophic bacteria are agents of microbial degradation. Elevated total bacterial populations may adversely affect municipal drinking water supplies by contributing to taste and odour problems, biological fouling and the persistence of pathogens.

A study was designed to examine the numbers of heterotrophic bacteria present in the sediments and the bottom waters at various locations along the St. Clair River. By doing so, a comparison could be made between the two media as well as between stations.

(b) Methods

Samples of bottom waters and sediments were collected from the eleven ecosystem stations (Figure 4.4.1) on August 26, 1986. These stations were selected at the onset of the study in order to maintain consistency between investigators collecting or deploying bioindicators. With the exception of the head and mouth transects, all the stations lie along the Canadian shoreline. Sediment samples were obtained by retaining the top 3 cm of a Shipek grab sampler. Water samples were collected from just above the sediment surface using a March 5C-MD submersible pump with teflon tubing. Samples were submitted to the MOE's London lab for the enumeration of heterotrophic bacteria. Results are summarized in Table 4.4.1.

(c) Results

Bottom water and sediment at the head of the river contained higher numbers of heterotrophic bacteria on the Canadian side of the river, compared to the American side. The same was true for the lower portion of the river near the mouth with the exception of the bottom water sample which had a higher count on the American side.

Heterotrophic bacterial counts from bottom waters along the Canadian shore increased from 2200 organisms/ml at the head of the St. Clair River to 10,500 organisms/ml at the mouth. A maximum of 17,500 organisms/ml was recorded immediately downstream of the mouth of Talfourd Creek.

Bottom waters along the American shore revealed increased bacterial densities from 110 organisms/ml at the head of the river to 13,000 organisms/ml at the mouth.

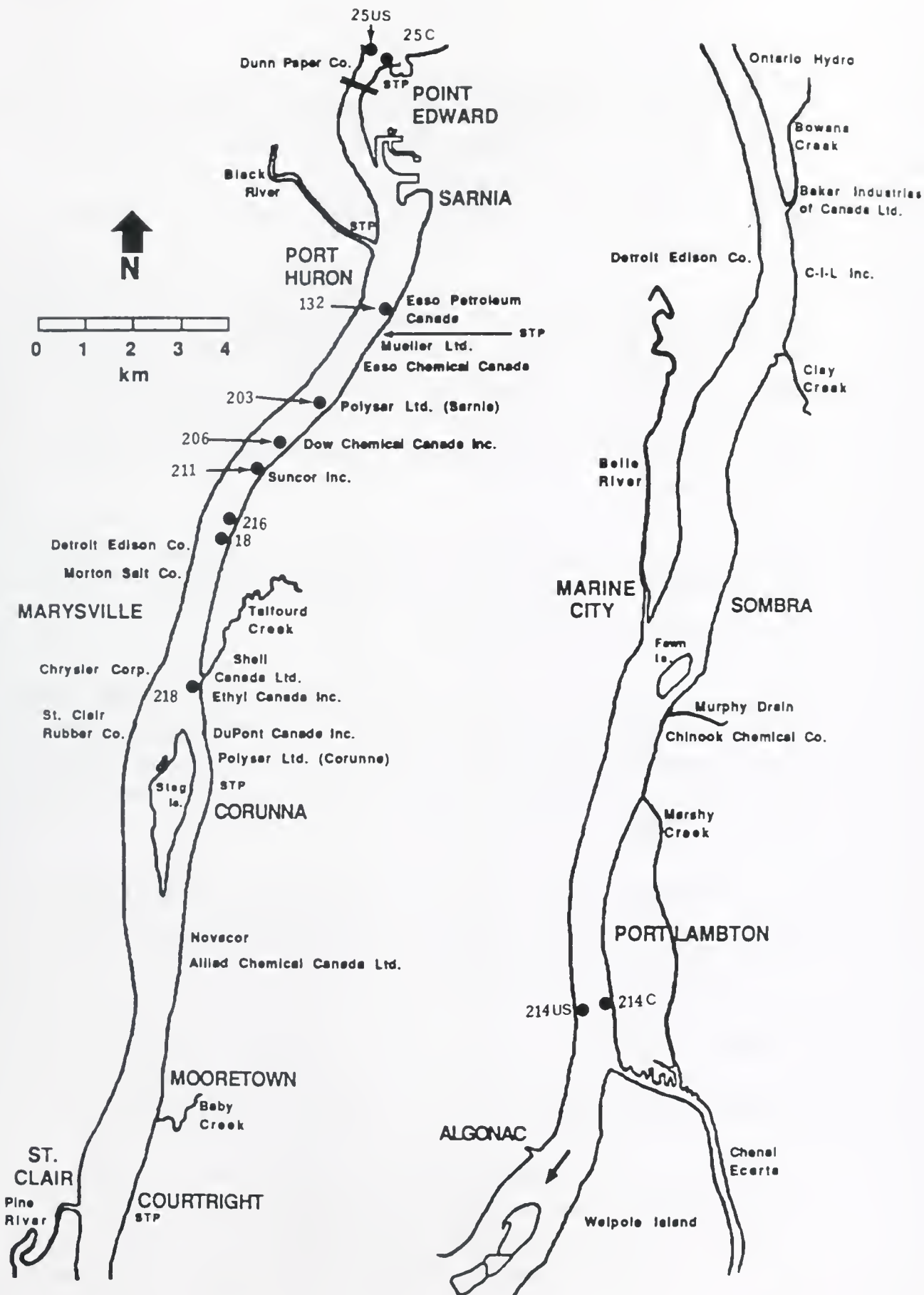


FIGURE 4.4.1 ECOSYSTEM STATION SAMPLING LOCATIONS

The Ministry of the Environment has established a recommended drinking water guideline of 500 bacteria/ml based on the geometric mean of 5 samples (MOE 1983). Water quality of the St. Clair River headwaters complies with this guideline along the American shoreline only. Waters along the entire length of the Ontario shore are degraded beyond the objective.

Sediment bacterial counts were typically an order of magnitude greater than the water counts. Bottom sediment bacteria increased from a density of 1500 organisms/gram wet weight (WW) at the head of the river on the Canadian shore to 450,000 organisms/gram (WW) at the mouth. A maximum of 500,000 heterotrophs/gram (WW) was recorded at station 216.

Along the American shoreline, bacterial densities increased from 700 heterotrophs/gram (WW) at the head of the river to 27,000 heterotrophs/gram (WW) at the mouth.

Although the monitoring of heterotrophic bacteria is not common, the single-day evaluation in this St. Clair River study provided some useful qualitative information. Both the water and sediment sample results support the possibility that bacterial organisms are utilizing organic compounds as a food source.

The significance of these findings are not entirely clear at this time; however, in view of the guideline exceedences, consideration must be given to appropriate means of control.

#### 4.4.2 Bacterial Slimes

##### (a) Introduction and Methods

Growths of bacterial slimes have previously been observed in the St. Clair River. Samples of this growth were collected during a 1977 St. Clair River benthic study and microscopically identified. The samples were found to contain a variety of filamentous slime producing



TABLE 4.4.1: HETEROTROPHIC BACTERIAL RESULTS FROM THE ST. CLAIR RIVER  
(ECOSYSTEM STATIONS) AUGUST 26, 1986

Station	Bottom Water Sample (per 1 mL)	Bottom Sediment Sample (per gram)
Stn. 25C	2,200	1,500
Stn. 25US	110	700
Stn. 132	16,000	165,000
Stn. 203	3,600	125,000
Stn. 206	8,000	140,000
Stn. 211	13,000	365,000
Stn. 216	6,000	500,000
Stn. 18	15,000	465,000
Stn. 218	17,500	160,000 (approx)
Stn. 214C	10,500	450,000
Stn. 214US	13,000	27,000



bacteria. More recently, growths were observed in the winter of 1985, during the monitoring of the Dow tetrachloroethylene spill clean-up.

Based on these historical sightings, a diver inspection of the Canadian shoreline from Sarnia Bay to Talfourd Creek was conducted the week of June 9-13, 1986. The bottom was surveyed for the presence of slime growths and outfalls were similarly inspected. All observations were recorded using an underwater video camera.

(b) Results

Very little slime growth was observed compared to observations from other years. The Polysar 66-inch sewer and an outfall from Esso Petroleum (Biox plant and wastes from the #11 and #13 separators) were discharging slime growths. A rough estimate of slime growth loadings from these two outfalls could be accomplished by screening out the slimes over a given time period and multiplying this quantity by the flow; however, this was not attempted.

Based on the general absence of growth in June, a fall sampling was planned. Slime growths had been previously observed to peak in the cooler months. A sampling run was attempted on October 30, 1986 by towing a net (1000 micron mesh size) 1 metre below the surface for a known period of time at various sites along the Canadian shore. Flow metres were fitted on the net (one inside and one outside the net's mouth opening) to permit a loading estimate.

A total of three tows were made. Each tow was carried out for approximately 10 minutes. None of the three tows accumulated any bacterial slime growths. Due to weather problems and other factors, no further attempts were made after the October 30 sampling run.

In general, visual evidence of bacterial slimes has indicated a water-quality problem. It would appear that the most pronounced

aquatic effects may arise through fouling of submerged stones and plants as well as degraded aesthetics. In future investigations of bacterial slimes, it may be advantageous to carry out very detailed evaluations of the localized growths. These detailed evaluations might include:

- a. microscopic examinations to speciate the bacteria,
- b. quantitative biomass assessment, and
- c. good co-ordination between the "in-river" findings and the industrial sources.

#### 4.4.3 Phytoplankton

##### (a) Contaminant Monitoring

Contaminants which enter the aquatic environment eventually enter one or more food chains. At the base of many food chains are the phytoplankton. Their vast diversity and abundance make them appropriate candidates for monitoring contaminants present in the water column.

A sampling effort designed to collect phytoplankton from the St. Clair River was carried out on July 30, 1986. Large volumes (68 litres) of water were collected 10 metres offshore at stations 202, 204 and 18 (Figure 4.2.15). These samples were size fractionated into greater than 20  $\mu\text{m}$  and less than 20  $\mu\text{m}$  fractions through filtration carried out by staff of the Federal Great Lakes Laboratory for Fisheries and Aquatic Science, in Burlington, Ontario c/o Dr. M. Munawar. This size was selected since it divides the phytoplankton into net plankton (greater than 20  $\mu\text{m}$ ) and nanno plankton (less than 20  $\mu\text{m}$ ). Zooplankton grazing rate studies indicate a preference for the nanno plankton which would therefore have greater implications on the food chain.

It should also be noted that these samples reflect total seston which includes all the inorganic and organic material suspended in the water column. Typically, total seston is comprised of 10 to 12 percent non-living material. The majority of the remaining living material usually consists of phytoplankton. Dr. M. Munawar (Pers. Comm.) suggested that 80% would be an appropriate estimate for the phytoplankton component of seston.

Subsequent analysis of these total seston fractions for polychlorinated biphenyls (PCBs), organochlorine pesticides and other trace organics was carried out by Dr. B.G. Oliver at the National Water Research Institute in Burlington. Results are summarized in Table 4.4.2.

Assessment of this limited data base was relatively inconclusive. Generally, one would expect to find higher concentrations of contaminants in the nanno plankton based on a greater surface area to volume ratio allowing increased adsorption. However, this was not the case. Hexachlorobenzene and octachlorostyrene concentrations were found to be consistently higher in the net plankton. The remaining parameters did not reflect an affinity for size.

Generally, the idea of monitoring phytoplankton (seston) for contaminants is sound and the technique used in doing so proved to be effective. Problems arose, however, when trying to interpret the results. It is believed that phytoplankton species identification would assist in the data interpretation, however, microscopic identification would be very time consuming and costly.

(b) Biomass

Determining phytoplankton biomass can be a costly and time consuming endeavour. To this end, it was hoped that a method could be developed to estimate phytoplankton biomass in the river by establishing a correlation with chlorophyll a.

TABLE 4.4.2 - CONTAMINANTS FOUND IN SESTON SAMPLES OBTAINED FROM THE  
ST. CLAIR RIVER - JULY 30, 1986

PARAMETER µg/g (dry weight)	202		STATION 204		18	
	<20µm	>20µm	<20µm	>20µm	<20µm	>20µm
1,4-Dichlorobenzene	38	-	1600	500	420	-
1,2-Dichlorobenzene	-	-	-	210	81	-
Hexachloroethane	0.9	21	120	57	12	22
1,2,4-Trichlorobenzene	22	27	120	28	37	27
Hexachlorobutadiene	-	72	670	550	200	360
Pentachlorobenzene	6.5	-	81	62	35	47
Hexachlorobenzene	6.4	53	1400	2700	420	1300
α - BHC	7.5	12	18	3.4	12	2
Octachlorostyrene	7.2	18	820	1100	290	610
PCB (Total)	340	460	3000	800	1100	640
DDT	7.5	-	3.9	4.6	13	13
DDD	-	-	-	-	27	22
DDE	17	28	75	15	31	29

In order to characterize the river, eight sampling sites were established; four along each shoreline between the head of the St. Clair River and the mouth (Figure 4.4.2). These locations were chosen in order to evaluate differences between shoreline chlorophyll a values and also to allow for the measurement of possible differences along the Canadian shoreline as a result of shoreline discharges.

In total, nine sampling runs were conducted over the period of May 15 to October 10, 1986 approximately on a bi-weekly basis. Each run consisted of the collection of Secchi disk readings, water samples of the euphotic zone (twice the Secchi disk reading) for the analysis of chlorophyll a and temperature readings. A summary of the average Secchi disk readings and chlorophyll a concentrations is illustrated in Figure 4.4.3.

To determine if a relationship between chlorophyll a and phytoplankton exists, data were examined from sampling carried out at the Lambton Area Water Supply System (located in Lake Huron near the head of the river). Chlorophyll a and phytoplankton data were plotted for the years 1976 to 1986 (approximately 25 samples yearly). A linear regression was carried out which did not show any significant correlation between the two. It was therefore not possible to calculate the phytoplankton biomass in the St. Clair River based solely on chlorophyll a values.

In an attempt to produce a rough estimate of the biomass, the yearly average phytoplankton results were examined from the Lambton Area Water Treatment Plant. Eleven years (1976 - 1986) of data were converted from aerial standard units (ASU) to grams per cubic metre using the following equation:

$$\text{ASU} \times 55 \div 467 = \text{biomass (grams/cubic metres)}$$

NOTE: equation was developed by the Ministry's Water Resources Branch (K. H. Nicholls)

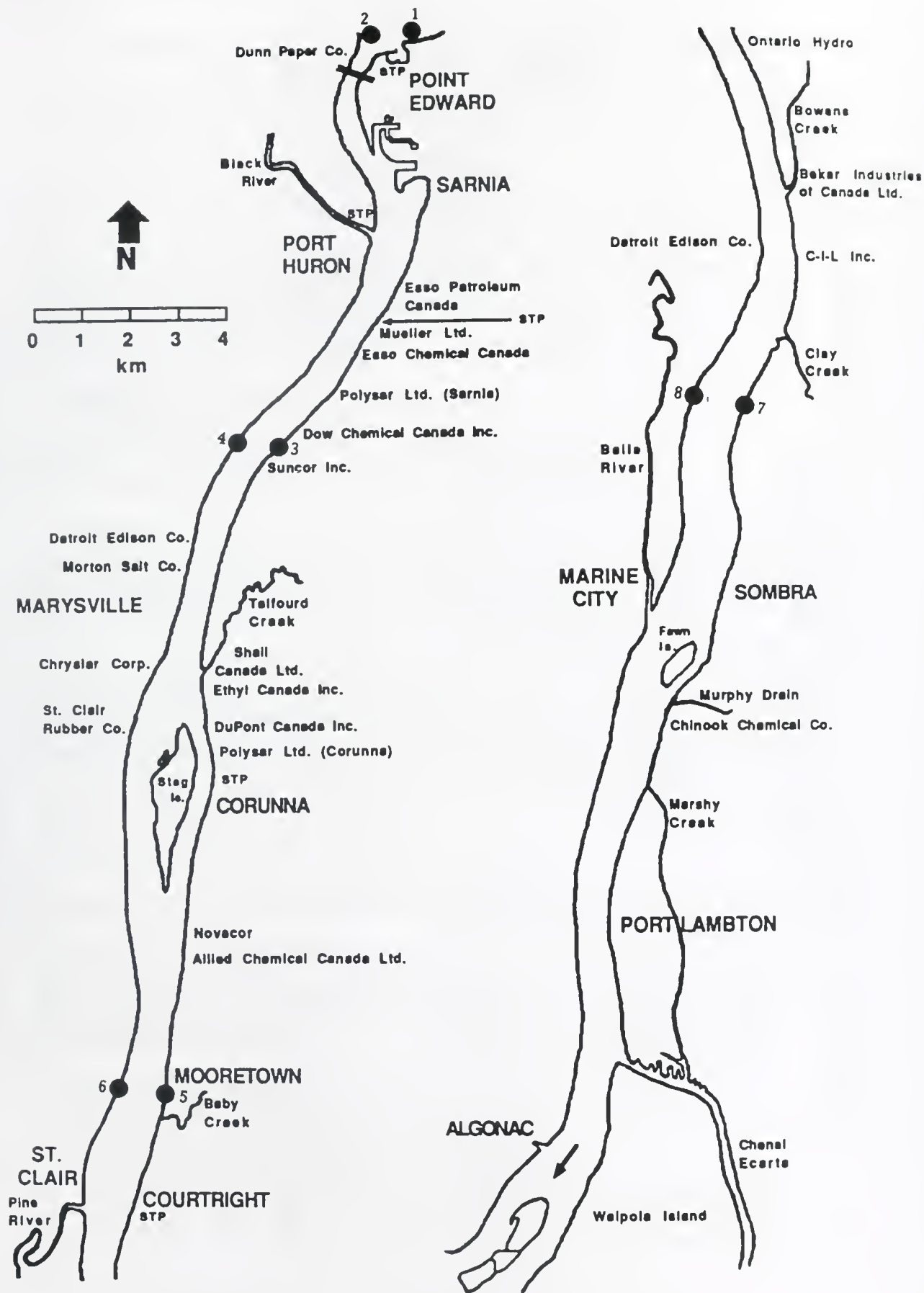


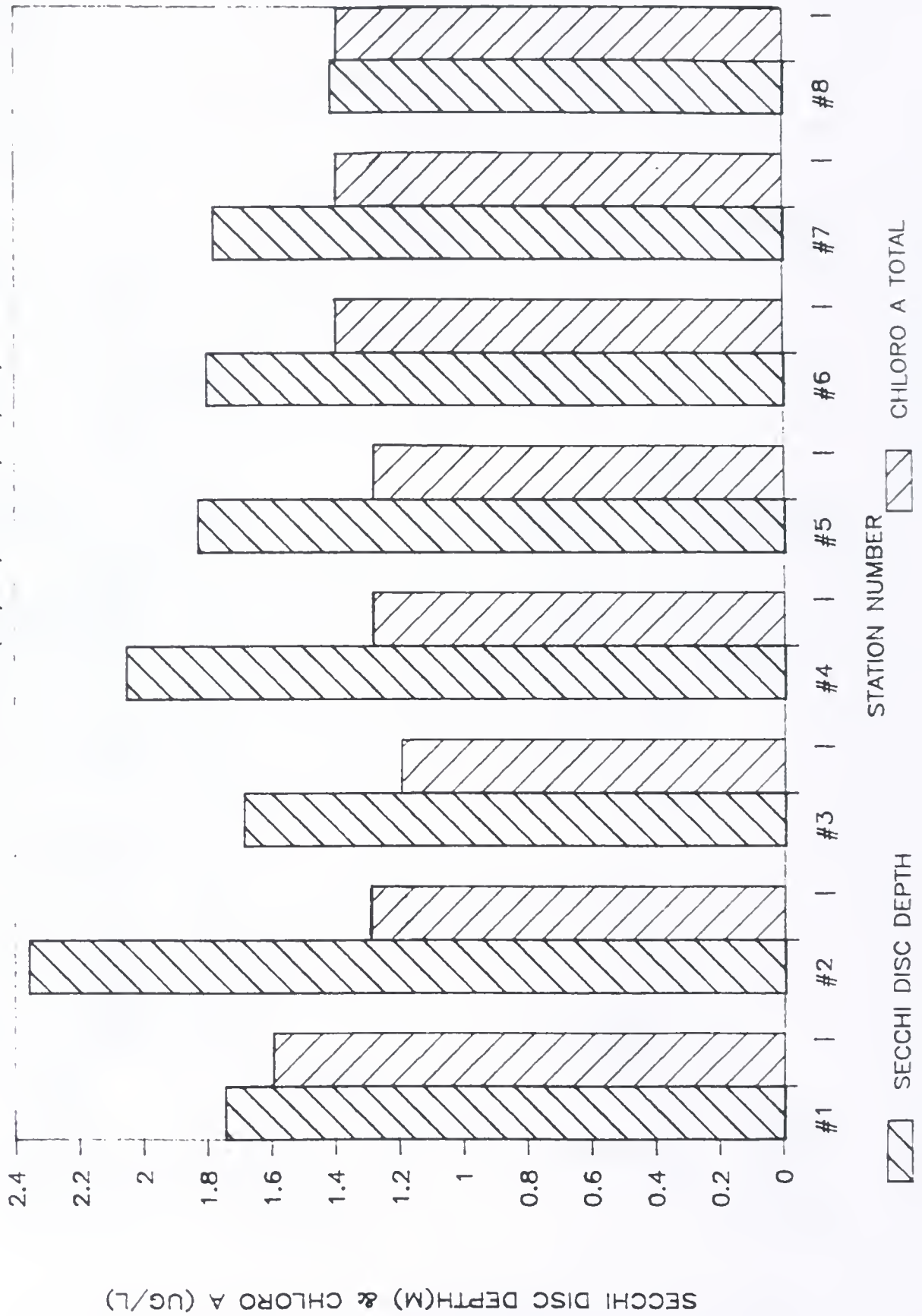
FIGURE 4.4.2 ST. CLAIR RIVER CHLOROPHYLL  
a STATION, 1986



FIGURE 4.4.3 SUMMARY OF SECCHI DISC CHLOROPHYLL  
a DATA: ST. CLAIR RIVER, 1986

# SECCHI DISC & CHLOROPHYLL A DATA

ON ST. CLAIR RIVER(15/05/86-10/10/86)





The average biomass estimate for that eleven year period was 0.975 grams per cubic metre.

If phytoplankton sampling is attempted on the St. Clair River in the future, it is suggested that weekly samples be collected and preserved with Lugol's iodine solution. These samples could later be concentrated at the Ministry's Toronto lab and an aliquot of the concentrate could then be examined and enumerated to estimate the biomass.

#### 4.4.4 Cladophora

##### (a) Methods

Cladophora samples were collected from shoreline sites (Figure 4.4.4) along the St. Clair River during July 22 - 24 and September 17 and 18, 1986. Sampling locations were selected based upon expected habitat suitable for growth of Cladophora as well as proximity to sites established for collection/exposure of other biological indicator species evaluated in the field program (ecosystem stations). Approximately 1 kg. wet weight of algae was collected at each site. The algae were washed with ambient water, squeezed dry, wrapped in absorbent paper and transported on ice to the MOE laboratory in Rexdale. The samples were then freeze dried, ground and submitted for analysis in triplicate.

Samples were analyzed for organic compounds (PCB/Organochlorine pesticides; chlorinated phenols and chlorinated benzenes) and elements (metals and nutrients). Samples were not submitted for volatiles analysis since this was deemed inappropriate due to the freeze drying during sample preparation.

Samples were obtained from the following sites in July:

- 1 - Point Edward (Ecosystem Station 25 CAN),
- 2 - Mueller Ltd. (200m downstream of Ecosystem Station 132),
- 3 - Esso Chemical (610m upstream of Ecosystem Station 203),

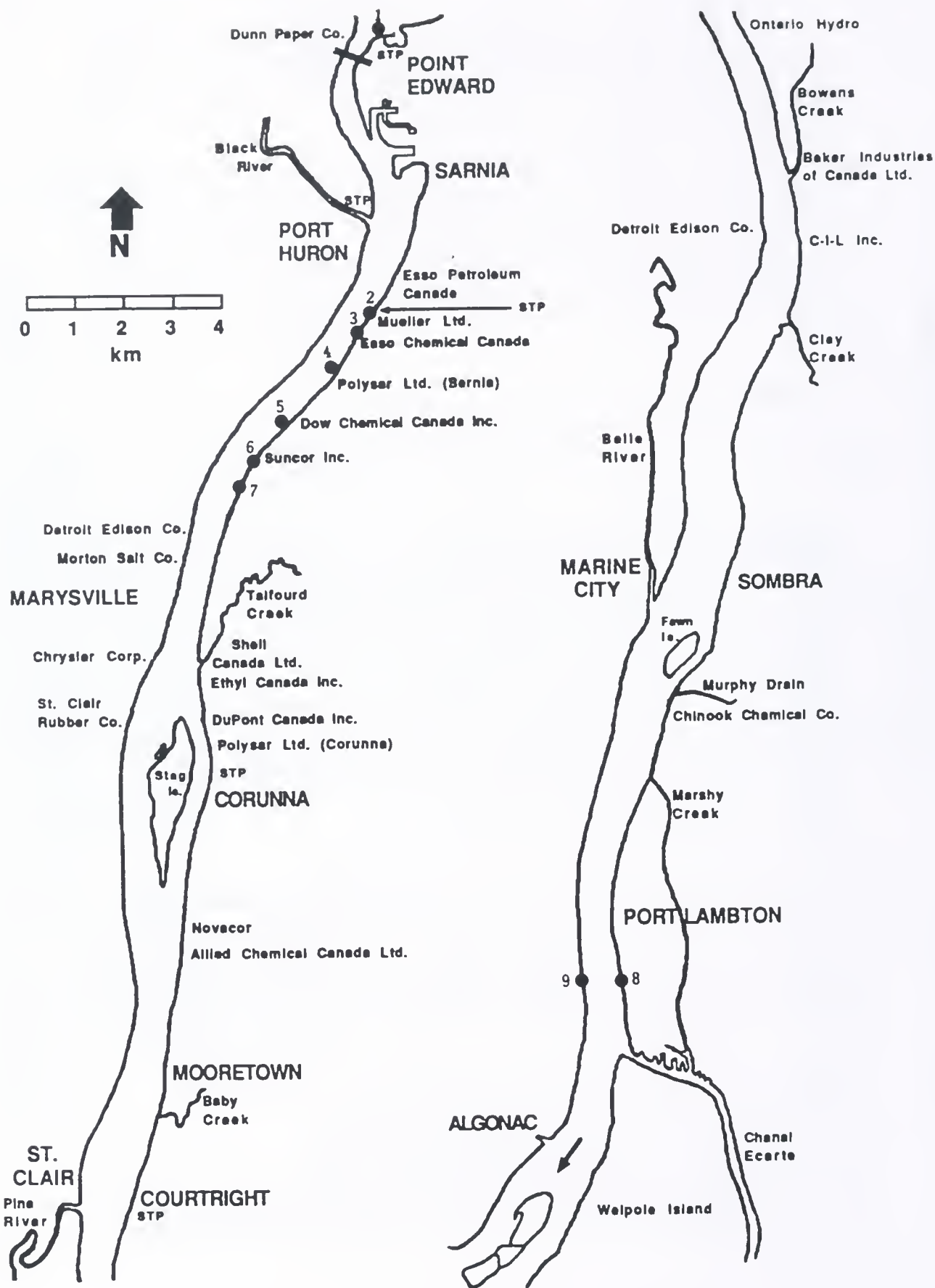


FIGURE 4.4.4 ST. CLAIR RIVER CLADOPHORA SAMPLING SITES, 1986

- 5 - Dow Chemical (Ecosystem Station 216 CAN),
- 6 - Suncor Inc. (Ecosystem Station 18 CAN),
- 7 - Across from Detroit Edison (225 - 575m downstream of Ecosystem Station 18 CAN)
- 8 - Port Lambton (1000m upstream of Ecosystem Station 214 CAN),
- 9 - Algonac State Park (1000m upstream of Ecosystem Station 214 USA).

Samples were obtained in September from:

- 2 - Mueller Ltd.;
- 3 - Esso Chemical;
- 4 - Polysar Ltd. (Ecosystem Station 203);
- 7 - Across from Detroit Edison,
- 9 - Port Lambton.

Sites at which no algae were available likely reflected locally toxic conditions.

Levels were below detection at all sites for the following parameters:

Organochlorine pesticides: Aldrin, Hexachlorocyclohexane ( $\alpha$  - BHC and  $\beta$ -BHC), Chlordane ( $\alpha$  and  $\gamma$ ), Endrin, Heptachlor, Mirex, o',p'-DDT, p',p'-DDD, p',p'-DDT.

Chlorinated Aromatic Compounds: Hexachloroethane, Pentachlorobenzene, Trichlorotoluenes (2,3,6; 2,4,5 and 2,6,a), Trichlorobenzenes (1,2,3; 1,2,4 and 1,3,5), and Tetrachlorobenzenes (1,2,4,5; 1,2,3,4 and 1,2,3,5).

Chlorophenols: Pentachlorophenol, Trichlorophenols (2,3,4; 2,4,5 and 2,4,6), and Tetrachlorophenols (2,3,4,5 and 2,3,5,6).

Levels of selected key contaminants in Cladophora are presented in Table 4.4.3. In the July survey, concentrations of both HCB and OCS were below detection (<1 ng/g) at all locations upstream of the site adjacent to Dow. Concentrations peaked at this location and were at or near detection at all sites downriver. In the September survey, low levels of OCS were detected at Polysar (3 ng/g), suggesting impact from the Cole drain. September results for HCB show peak levels at Station 7 (across from Detroit Edison) indicative of persistent upstream loadings.

The results of the July survey indicate elevated HCB levels at Dow and Suncor, with downstream impact to Port Lambton. In the September survey, levels were highest (Dow station not sampled) at Polysar.

As Cladophora have not previously been sampled in the St. Clair River system for contaminant analysis, no temporal trends can be assessed. However, in general, Cladophora results tend to substantiate the findings of other biomonitoring studies. There are no guidelines for acceptable contaminant levels in Cladophora.

#### 4.4.5 Macrophytes

##### (a) Determination of Biomass

Information on submerged aquatic macrophyte biomass was required for modelling purposes. An estimate of macrophyte biomass was essential for producing a contaminant mass balance in the exposure sub-model of WASTOX. To determine the significance of macrophytes in the uptake and storage of contaminants, biomass and contaminant monitoring were necessary to enable a calibrated chemical partitioning coefficient. In order to estimate this biomass, data on the distribution and relative abundance of submerged aquatic macrophytes must be studied. Such a study can be extremely costly and time consuming.

TABLE 4.4.3 - CONCENTRATION OF OCS, HCB AND HCB<sub>D</sub> (ng/g) DRY WEIGHT  
IN CLADOPHORA SAMPLED IN THE ST. CLAIR RIVER IN  
JULY AND SEPTEMBER 1986

<u>Station</u>	OCS		HCB		HCB <sub>D</sub>	
	July	Sept.	July	Sept.	July	Sept.
1 Point Edward	<1	-	<1	-	<1	-
2 Mueller Ltd.	<1	<1	<1	<1	<1	<1
3 Esso Chemical	<1	<1	<1	<1	<1	<1
4 Polysar Ltd.	-	3	-	<2	-	10
5 Dow Chemical	13	-	50	-	10	-
6 Suncor Inc.	<1	-	6	-	23	-
7 Across from Detroit Edison	3	2	<7	20	7	<1
8 Port Lambton	3	<2	3	<2	4	2
9 Algonac	<1	-	<1	-	<1	-

This information had been recently documented by the U.S. Fish and Wildlife Service in two large scale studies on the distribution and relative abundance of macrophytes; a 1978 survey (D. Schloesser and B. Manny) and a 1983-84 survey (P. Hudson). In order to avoid duplication of effort, it was decided that the data generated from these two surveys could serve as the basis for estimating biomass as they would likely be representative of conditions present in the river in 1986.

These surveys consisted of sampling the macrophytes by use of grapnel lined with a 1-cm square mesh cloth. At each station the grapnel was dragged along the bottom for a distance of 10 metres. This was completed six times at each station. A variety of patterns were employed depending on the width of the littoral zone. Macrophytes were collected and pooled from the six drags to provide a sample from which the distribution, relative abundance and density were determined.

Personal communications with D. Schloesser and P. Hudson resulted in two independent estimates of total biomass for the St. Clair River. D. Schloesser produced an estimate of 1663 metric tonnes (mt) ash free dry weight (AFDW) per year. This covered the 0 to 18 foot depth contour interval. P. Hudson produced an estimate of 2290 mt AFDW/yr which included a turnover rate of 1.25. Hudson's estimate covered the 0 to 12 foot contour interval.

If Schloesser's estimate of 1663 mt AFDW/yr is multiplied by Hudson's turnover rate (1.25) the result (2080 mt AFDW/yr) compares quite closely to Hudson's estimate of 2290 mt AFDW/yr. Also it is likely that the area between the 12-18 foot contour interval probably accounted for less than 10 percent of the area. The agreement between these estimates indicates the stability of the biomass production over the period from 1978 to 1984.

(b) Contaminant Monitoring

Submerged aquatic macrophytes are known to reflect contaminant loadings through biological uptake studies. For this reason, a sampling program was designed to collect macrophytes from various stations along the upper St. Clair River, in the vicinity of the "Chemical Valley".

Aquatic macrophytes were collected by the MOE using the grapnel method which consisted of throwing the grapnel out (10 metres) then slowly retrieving it along with the acquired sample. In total, ten species of plants were collected (in duplicate) from seven stations (Figure 4.4.5). Station locations and species compositions are listed below:

STATION LOCATION	SPECIES	SAMPLE NUMBER
1. Sarnia Bay	<u>Myriophyllum</u>	1
	<u>Vallisneria</u>	2
2. d/s Esso Petroleum	<u>Potamogeton gramineus</u>	3
3. d/s Polysar Ltd.	" "	4
4. d/s Dow Chemical	" "	5
5. d/s Suncor Inc.	" "	6
6. d/s Talfourd Creek	" "	7
	<u>Myriophyllum</u>	8
7. N.W. Shore Stag Island	<u>Potamogeton gramineus</u>	9
	<u>Myriophyllum</u>	0

d/s - downstream



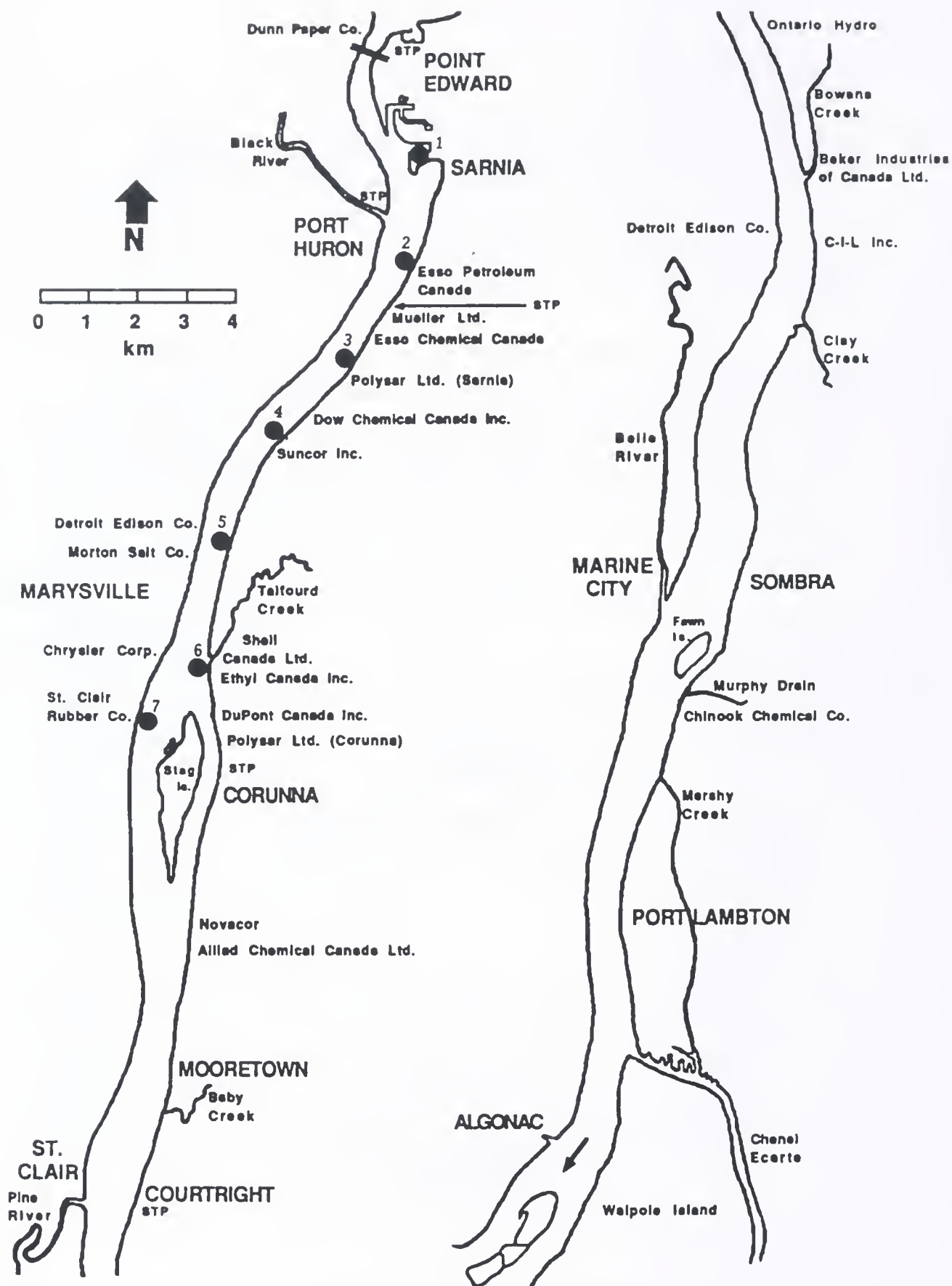


FIGURE 4.4.5 ST. CLAIR RIVER, MACROPHYTE COLLECTION SITES , 1986

Ten samples were freeze-dried and ten samples were air-dried to evaluate the effects of sample preparation on concentrations of organic chemicals detected in plant tissues. All samples were submitted for organochlorine pesticides, polychlorinated biphenyls (PCBs) and chlorinated benzenes. Table 4.4.4 presents the analytical results for those compounds which were found to be present in the plant tissues. All remaining compounds were below detectable levels.

The data presented in Table 4.4.4 is difficult to interpret. In some cases (e.g. OCS and HCB), the method of sample preparation appears to affect contaminant concentration. In the case of HCB; however, preparation method does not appear to be a factor. Interpretation is also made difficult because of the evidence of contamination upstream of most of the industrial activity (e.g. p',p'-DDE, OCS, HCB) at station 1 in Sarnia Bay.

While macrophytes appear to produce results which are somewhat erratic, they aid in assessing results from other biomonitors, by producing a more complete multi-media assessment.

#### 4.4.6 Benthic Invertebrate Enumeration

##### (a) Introduction

The environmental quality of the Ontario nearshore area along the St. Clair River was assessed in the spring of 1985 by means of an intensive benthic invertebrate and sediment chemistry survey. The purpose of the study was to document the spatial extent of impacts from industrial and municipal waste discharges, identify temporal changes from previous surveys (MOE 1979) and to determine the effectiveness of industrial and municipal abatement programs that have been implemented since the late 1970's on the benthic community.

Benthic invertebrates have long been recognized for their value as indicators of environmental quality because:

TABLE 4.4.4 - SUMMARY OF THE ANALYTICAL RESULTS FOR MACROPHYTE SAMPLES  
COLLECTED FROM THE ST. CLAIR RIVER - SEPTEMBER 23, 1986

Parameter	Sample No.	Stn. No.	Plant Species	Freeze-Dried	Air-Dried
P'P'-DDE ng/g	1	1	Myriophyllum	2	6
	2	1	Vallisneria	L 1	25
	3	2	Potamogeton gramineus	L 1	13
	4	3	P. gramineus	L 1	2
	5	4	P. gramineus	L 1	2
	6	5	P. gramineus	L 1	11
	7	6	P. gramineus	L 1	L 1
	8	6	Myriophyllum	L 1	3
	9	7	P. gramineus	2	L 1
	10	7	Myriophyllum	2	L 1
Heptachlorepoide ng/g	1	1	Myriophyllum	L 1	L 1
	2	1	Vallisneria	4	L 1
	3	2	Potamogeton gramineus	6	L 1
	4	3	P. gramineus	5	L 1
	5	4	P. gramineus	3	L 1
	6	5	P. gramineus	3	1
	7	6	P. gramineus	4	L 1
	8	6	Myriophyllum	3	L 1
	9	7	P. gramineus	4	L 1
	10	7	Myriophyllum	4	L 1
Octachlorostyrene ng/g	1	1	Myriophyllum	L 1	L 1
	2	1	Vallisneria	L 1	26
	3	2	Potamogeton gramineus	L 1	11
	4	3	P. gramineus	L 1	10
	5	4	P. gramineus	L 1	36
	6	5	P. gramineus	L 1	32
	7	6	P. gramineus	L 1	3
	8	6	Myriophyllum	L 1	L 1
	9	7	P. gramineus	L 1	4
	10	7	Myriophyllum	L 1	4
Hexachlorobutadiene ng/g	1	1	Myriophyllum	L 1	L 1
	2	1	Vallisneria	L 1	2
	3	2	Potamogeton gramineus	L 1	L 1
	4	3	P. gramineus	32	3
	5	4	P. gramineus	33	7
	6	5	P. gramineus	10	6
	7	6	P. gramineus	L 1	L 1
	8	6	Myriophyllum	L 1	4
	9	7	P. gramineus	10	L 1
	10	7	Myriophyllum	L 1	L 1

L - less than

TABLE 4.4.4 (cont'd)

Parameter	Sample No.	Stn. No.	Plant Species	Freeze-Dried	Air-Dried
Pentachlorobenzene ng/g	1	1	Myriophyllum	L 1	L 1
	2	1	Vallisneria	L 1	8
	3	2	Potamogeton gramineus	L 1	5
	4	3	P. gramineus	L 1	L 1
	5	4	P. gramineus	3	2
	6	5	P. gramineus	2	2
	7	6	P. gramineus	L 1	L 1
	8	6	Myriophyllum	L 1	7
	9	7	P. gramineus	2	L 1
	10	7	Myriophyllum	L 1	2
Hexachlorobenzene ng/g	1	1	Myriophyllum	4	6
	2	1	Vallisneria	2	L 1
	3	2	Potamogeton gramineus	6	21
	4	3	P. gramineus	38	8
	5	4	P. gramineus	16	31
	6	5	P. gramineus	26	19
	7	6	P. gramineus	L 1	4
	8	6	Myriophyllum	L 1	41
	9	7	P. gramineus	10	L 1
	10	7	Myriophyllum	L 1	10
Hexachloroethane ng/g	1	1	Myriophyllum	L 1	L 1
	2	1	Vallisneria	L 1	2
	3	2	Potamogeton gramineus	L 1	L 1
	4	3	P. gramineus	L 1	L 1
	5	4	P. gramineus	L 1	L 1
	6	5	P. gramineus	L 1	L 1
	7	6	P. gramineus	L 1	L 1
	8	6	Myriophyllum	L 1	L 1
	9	7	P. gramineus	L 1	L 1
	10	7	Myriophyllum	L 1	L 1

L - less than

- a) they are abundant in most aquatic habitats, living on or in the substrate;
- b) they are readily collected and identified;
- c) they show a wide range of tolerances to various degrees and types of pollutants;
- d) they generally remain in a localized area because of their restricted mobility and habitat preference; and
- e) they are continuously subjected to the full rigor of the local environment throughout their aquatic life cycle, which may vary from weeks to years.

Thus, unlike water chemistry data, which indicate the total concentration of contaminants in the environment at a point-in-time, benthic invertebrate data indicate the integrated effect of all environmental variables during the period of time that the invertebrates have lived in the habitat. The use of in-situ organisms eliminates the need for any assumptions about the toxicity of contaminant concentrations in order to determine their effects on aquatic life. Thus, the benthic invertebrate fauna can be used to directly measure the effects of environmental stresses on aquatic systems, regardless of the frequency or intensity, while water and sediment chemistry can aid with explaining possible causes for observed biological impacts. The multivariate analysis of benthic invertebrate and sediment chemistry data, therefore, provides an effective "cause-and-effect" protocol for assessing the impact of point or diffuse sources on the environmental quality of receiving waters.

(b) Methods

Three benthic invertebrate samples were collected at each of 78 sampling sites from May 22 to June 12, 1985 using a Ponar grab sampler, which enclosed an area of 516 cm<sup>2</sup>. Each sample was washed in

a screen pail containing a mesh screen with a 600 µm aperture. The organisms were separated live from the retained debris and sediment, placed in 30 mL bottles and preserved with 80% ethanol. The invertebrates were taxonomically identified and enumerated by Ron Griffiths of the MOE London Regional Office.

In conjunction with the invertebrate sampling, a Shipek grab sampler was used to collect surface sediment samples for chemical and grain size analyses. This sediment data has been reported elsewhere (UGLCCS 1989). The field sampling methods have been described by the Ministry of the Environment (1985). The sediment samples were submitted to the Ministry of the Environment's Rexdale Laboratory for analyses of total metals, nutrients, organic matter, oils and greases, chlorinated hydrocarbons and grain size.

(c) Results and Discussion

Non-Hierarchical Classification Analysis (Gauch 1982) identified seven major invertebrate assemblages or communities in the river (Table 4.4.5). An analysis of the composition of the communities and a discriminant analysis (Legendre and Legendre 1983) of the sediment chemistry data (see Griffiths 1989) suggested that communities 1, 2, 3 and 4 reflected non-stressed environmental conditions of various habitats in the river; the fauna of Community 1 characterized unstable, sand habitats at the head of the river; the fauna of Community 2 characterized erosional habitats along the bends of the river; fauna of Community 4 characterized depositional habitats; and the fauna of Community 3 characterized habitats with intermediate flow and sediment conditions along the runs of the river (Figures 4.4.6a and 4.4.6b). In contrast, Communities 5, 6 and 7 reflected degraded environmental conditions possibly as a result of organic enrichment, and/or elevated sediment concentrations of heavy metals, such as zinc and mercury (Table 4.4.6) and chlorinated hydrocarbons (Table 4.4.7). Of these, Community 7 reflected the poorest environmental quality conditions. The dominance of pollution-tolerant species (e.g. L. hoffmeisteri, Elimia livescens (= Goniobasis)), reduced species



richness and low invertebrate density (Table 4.4.5) suggest that Community 7 occurred in areas stressed by toxic conditions. Elevated sediment concentrations of heavy metals, oils and greases, and/or chlorinated hydrocarbons (Tables 4.4.6 and 4.4.7) may account for these conditions.

Based on the distribution of these communities in the river, a zone of degraded environmental quality was evident along the Canadian shoreline from downstream of Esso Petroleum Canada to downstream of Allied Chemical Canada Ltd. (Figure 4.4.7). The presence of Community 7 along the waterfront of Dow Chemical Canada Inc. suggests that toxic biological conditions occurred along this nearshore section of the river. Waste discharges from Dow Chemical are known to include many potentially toxic substances, including aromatics, chlorinated hydrocarbons, styrene, ethylbenzene, phenols and heavy metals (Ministry of the Environment 1979, DOE/MOE 1986). In addition, periodic spills of acids, petrochemicals, oils, caustics, etc. from Dow Chemical and upstream industries (DOE/MOE 1986; Griffiths 1985) have probably contributed to the observed biological impairment.

Although waste discharges from the chemical valley impaired approximately 12 km of the river along the Canadian shoreline in 1985, this zone of impairment is considerable less than the 21 km observed in 1977 (Figure 4.4.8) (Ministry of the Environment 1979a; Griffiths 1978). Implementation of industrial and municipal abatement programs since the late 1970's has apparently resulted in the "reclamation" of 9 km of the river.



TABLE 4.4.5 - SPECIES COMPOSITION (MEAN NUMBER PER 516 CM<sup>2</sup>) OF BENTHIC COMMUNITIES 1-7 IN THE ST. CLAIR RIVER, MAY 1985 (P DENOTES A MEAN DENSITY OF LESS THAN 1 INDIVIDUAL PER SAMPLE).

	Benthic Community						
	1	2	3	4	5	6	7
AQUATIC CATERPILLARS:							
Pyralidae			P		P	P	
BEETLES:							
Dubiraphia		P		P			
CADDISFLIES:							
Cheumatopsyche		7.7	P	P		P	P
Hydropsyche		1.8	P	P	P	P	
Protoptila		1.0					
Lepidostoma				P			
Ceraclea		P					
Oecetis				P			
Neureclipsis		P	P	P			
DAMSELFLIES:							
Argia						P	
Coenagrion						P	
DRAGONFLIES:							
Gomphurus				P			
MAYFLIES:							
Baetisca		P		P	P	P	
Caenis		1.2	4.5	1.2			
Ephemerella		P	P	P	P		
Serratella		P					
Hexagenia		P	2.8	12.3	P	P	P
Stenonema		1.2	P		P		P
STONEFLIES:							
Perlesta placida		P					
TRUE FLIES:							
Ceratopogonidae		P	P	2.9			
Chernovskiiia	3.4						
Chironomus	P		1.8	13.3			
Cryptochironomus	2.1	P	8.8	33.0	P	P	P
Demicryptochironomus		1.1	P	2.4	P		
Dicrotendipes		P	P	P	P		
Harnischia			1.0	4.6	P	P	
Parachironomus		P	P	P	P		
Paracladopelma		P	P	2.6	P		
Paratanytarsus		P	P				

(cont'd)

TABLE 4.4.5 (Cont'd)

	Benthic Community						
	1	2	3	4	5	6	7
Paratendipes		P		P		6	
Phaenopsectra		P	2.6	P	P	P	
Polypedilum		P	16.2	30.7	P	P	
Pseudochironomus			P				
Rheotanytarsus				2.0			
Saetheria	3.0						
Stictochironomus			2.7	7.9			
Tanytarsus		P	3.5	15.3	P		
Tribelos		P	18.0	13.7	P	P	
Xenochironomus		P	P				
Pothastia			P	P		P	
Epicocladus				P			
Heterotrissocladus				P			
Cricotopus		P	P	P	P	1.2	P
Nanocladus		P		P		P	
Parakiefferiella	P		P				
Monodiamesa	P	P	1.0	4.0	P		
Ablabesmyia			P	3.1	P		
Djalmabatista		P	P				
Procladius		P	11.3	67.1	6.7	3.6	P
Conchapelopia		P			P	P	
Empididae	P	1.2	P	P	P	P	
Psychodidae						P	
CRUSTACEANS:							
Gammarus fasciatus		1.4	6.2	4.4	1.2	P	
Pontoporeia hoyi		P	P	P			3.6
Hyalella azteca		P	P	P	P	P	
Asellus				P		P	
CLAMS:							
Pisidium	P	P	6.2	5.5	11.3	2.3	
Sphaerium		P	P	P	P		
SNAILS:							
Amnicola		P	9.4	2.2	21.9	7.1	P
Probythinella lacustris			P	P			
Fossaria			P				
Pseudosuccinea columella			P		P	P	
Physella gyrina		1.0	2.7	P	14.4	4.0	P
Gyraulus		P	1.8	P	P	P	
Elimia livescens		6.4	2.6	P	4.2	P	2.4
Valvata piscinalis		P	3.2		13.3	5.1	
V. tricarinata		P	3.6	P	12.7	1.6	

(cont'd)

TABLE 4.4.5 (Cont'd)

	Benthic Community						
	1	2	3	4	5	6	7
LEECHES:							
Mooreobdella microstoma					2.0	P	
Pisicolidae		P					
WORMS:							
Lumbricidae		P	P	P			
Stylodrilus herringianus		P	1.2	P	1.5		
Naididae		P	5.3	4.0	4.7	6.1	
Aulodrilus americanus			P	P			
A. pleuriseta			P		P		
Ilyodrilus templetoni			1.8	1.2	4.8	9.2	
Isochaetes freyi				P			
Limnodrilus angustipenis			P	P			
L. cervix			1.5		P	45.7	
L. claparadianus		P	3.7	3.9	1.8	1.2	
L. hoffmeisteri		3.8	31.2	12.3	229.4	327.7	7.7
L. maumeensis			P	4.9			
L. udekemianus		P	1.4	3.1	2.2	15.3	P
Potamotheix moldaviensis			1.1	3.4	P	P	
P. vejdoskyi			P	P			
Quistadrilus multisetosus			2.6	8.9	20.7	15.5	P
Spirosperma ferox		P	17.3	9.6	4.4	P	
Tubifex ignotus						P	
T. tubifex						10.5	
PROBOSCIS WORMS							
Prostoma		P	P	P	P	P	P
FLATWORMS		4.5	4.3	2.5	3.1	P	
MEAN NUMBER OF TAXA	2.6	8.9	15.3	17.5	12.9	9.4	3.0
MEAN DENSITY OF ORGANISMS	9.9	47.3	216.6	331.9	489.9	602.1	17.1

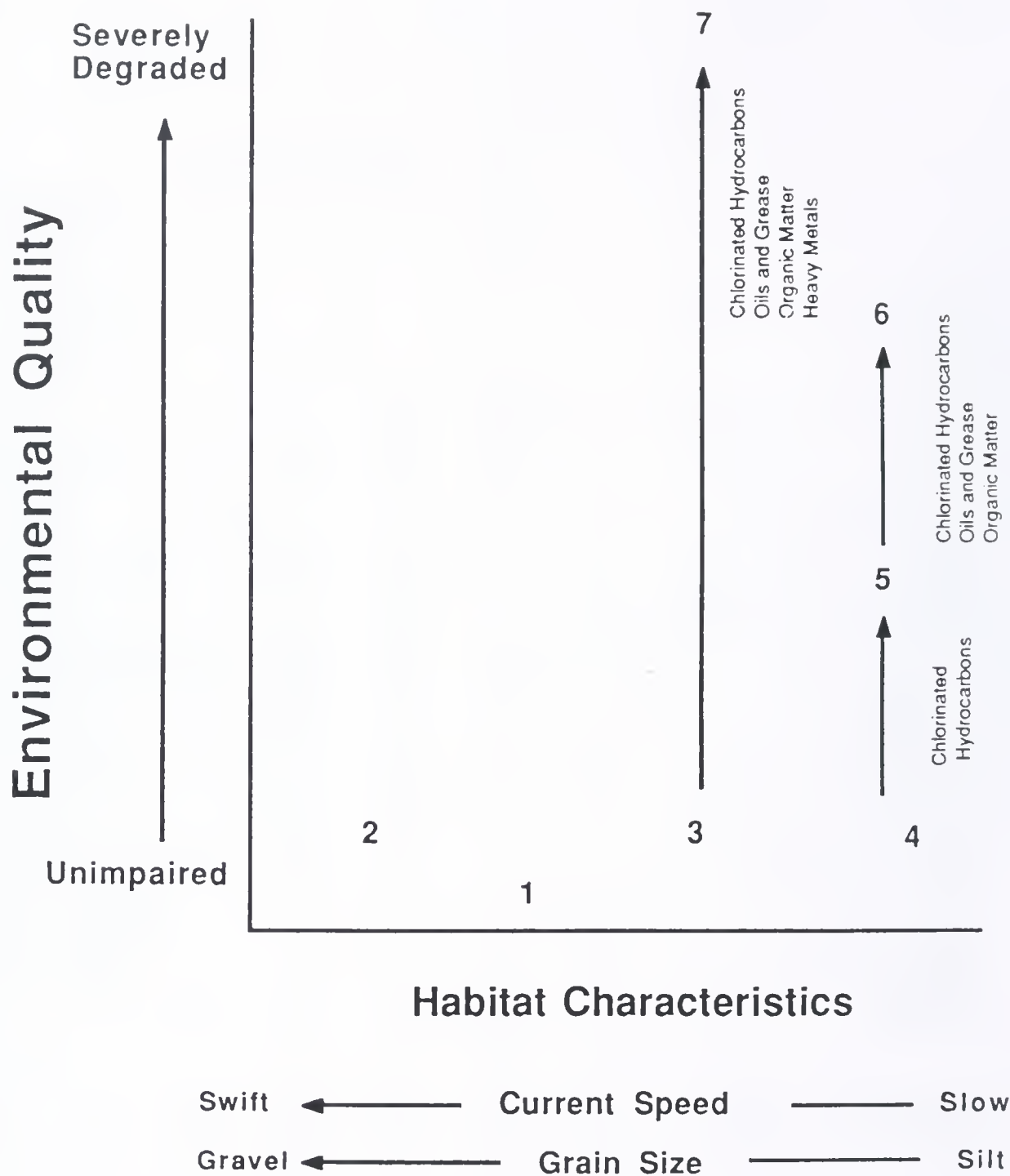


FIGURE 4.4.6a: Interpretation of benthic invertebrate communities 1-7 in terms of environmental quality and habitat.

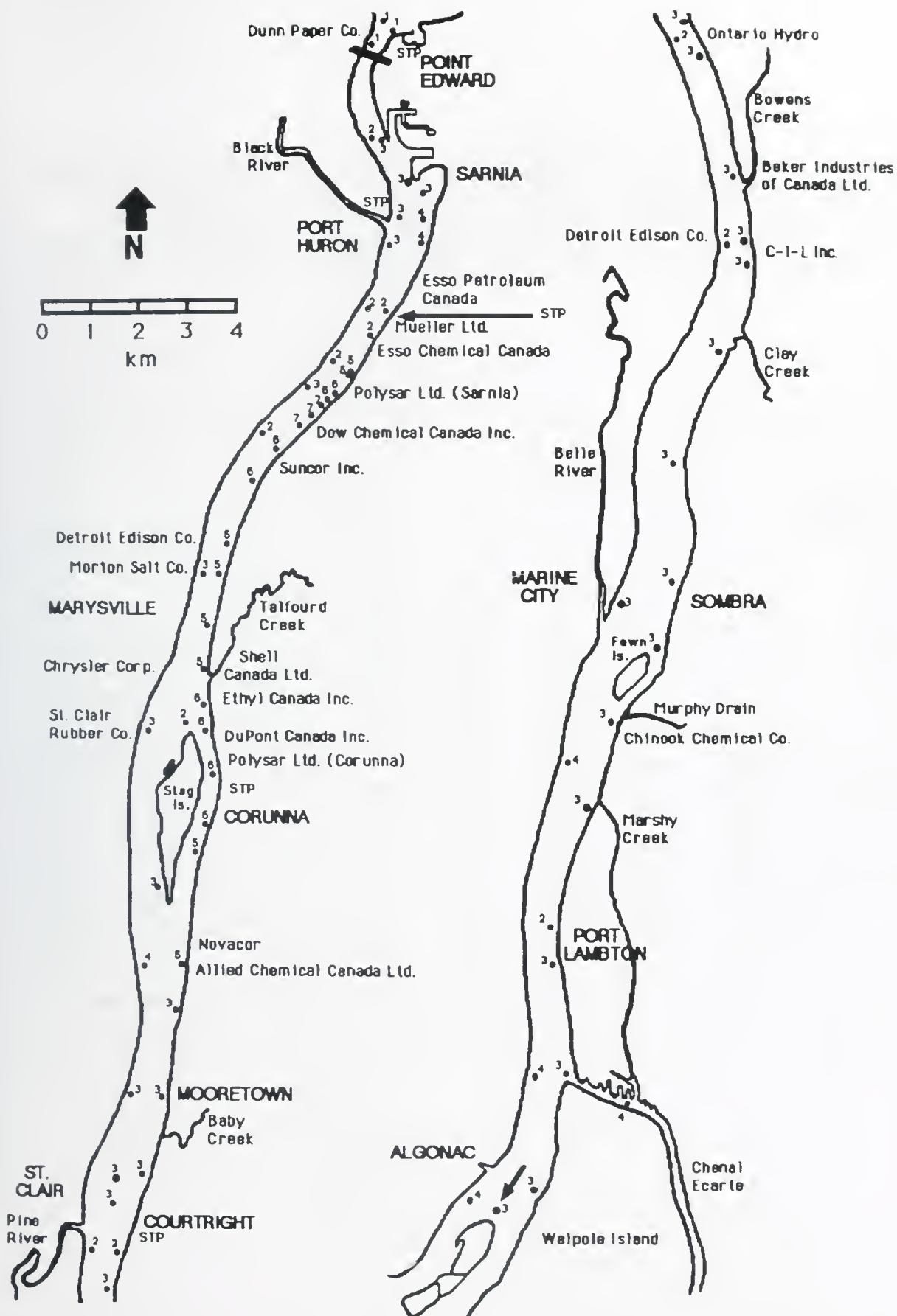


FIGURE 4.4.6b: May 1985 Benthic study station locations. Distribution of benthic invertebrate communities in the St. Clair River. Numbers refer to benthic communities listed in table 4.4.5.

TABLE 4.4.6 - MEAN VALUES OF PHYSIOCHEMICAL SEDIMENT VARIABLES ASSOCIATED WITH BENTHIC COMMUNITIES 1-7 FROM THE ST. CLAIR RIVER, MAY 1985.  
ALL VALUES ARE EXPRESSED IN mg/kg UNLESS OTHERWISE STATED.  
SEE TABLE 4.4.5 FOR THE TAXONOMIC COMPOSITION OF THE COMMUNITIES.

	Benthic Community						
	1	2	3	4	5	6	7
Iron (g/kg)	3.87	16.34*	8.18	12.63*	8.31	8.33	10.11*
Manganese (g/kg)	0.09	0.21	0.16	0.25	0.19	0.17	0.20
Aluminum (g/kg)	1.36	5.90	4.05	6.28	4.39	3.79	2.48
Arsenic	1.83	7.46	4.15	6.56	5.70	5.03	5.17
Cobalt	2.19	6.49	4.80	6.19	5.35	5.43	6.63
Chromium	6.37	18.88	13.59	17.53	16.24	8.82	20.90
Copper	4.54	43.08*	16.92	29.80*	19.40	29.90*	74.44*
Mercury	0.02	0.19	0.43*	0.11	2.11*	4.78*	15.03*
Nickel	2.53	13.67	8.25	12.14	7.94	8.81	21.79
Lead	2.22	34.92	16.52	17.47	22.28	69.66*	21.89
Zinc	11.32	45.15	34.94	54.75	65.65	67.64	96.73
Oils and Greases (g/kg)	0.07	0.52	0.48	0.88	0.63	2.54*	2.03*
Loss-on-Ignition (g/kg)	2.91	12.78	8.92	17.62	13.30	25.49	18.12
Total Organic C (g/kg)	5.00	8.28	7.39	13.62	11.06	19.52	13.41
Total Phosphorus (g/kg)	0.10	0.22	0.21	0.29	0.23	0.26	0.27
Total Kjeldahl N (g/kg)	0.13	0.36	0.35	0.71	0.45	0.69	0.37
Grain Size: % Gravels	0.60	67.00	0.70	0.00	25.30	7.40	45.20
% Sands	98.40	32.00	79.20	51.80	35.80	52.00	46.90
% Silts&Clays	1.00	1.00	20.10	48.20	38.90	40.60	7.90

\* mean sediment concentration exceeds MOE dredging guidelines for disposal in open waters.

TABLE 4.4.7 - OCCURRENCE (%) AND MAXIMUM MEASURED CONCENTRATIONS ( $\mu\text{g/kg}$  DRY WEIGHT) OF ORGANOCHLORINE COMPOUNDS IN SEDIMENTS ASSOCIATED WITH BENTHIC COMMUNITIES IN THE ST. CLAIR RIVER, MAY, 1985. NUMBER OF SAMPLING STATIONS NOTED IN BRACKETS BELOW EACH COMMUNITY.

	Benthic Community							
	4		5		6		7	
	(9)		(9)		(6)		(3)	
	%	max.	%	max.	%	max.	%	max.
Hexachlorobenzene	89	148	88	1131	100	1871	100	3280*
Dieldrin	56	6	78	5	67	12	33	13*
p',p'-DDT	0	ND	11	5	0	ND	33	25*
p',p'-DDD	11	5	0	ND	0	ND	33	50*
p',p'-DDE	33	2	50	49*	83	22	100	3
DMDT Methoxychlor	0	ND	11	10	33	100	33	170*
Endosulfan I	0	ND	11	3	0	ND	0	ND
Endosulfan II	0	ND	11	98*	17	50	33	8
Endosulfan sulfate	11	5	11	5	50	40*	33	10
alpha, gamma - BHC	0	ND	11	7	0	ND	33	5
Heptachlorepoxyde	0	ND	0	ND	67	10	33	26*
Aldrin	0	ND	38	2	33	3	0	ND
Oxychlorthane	0	ND	11	2	0	ND	0	ND

ND non-detectable

\* greatest measured concentration



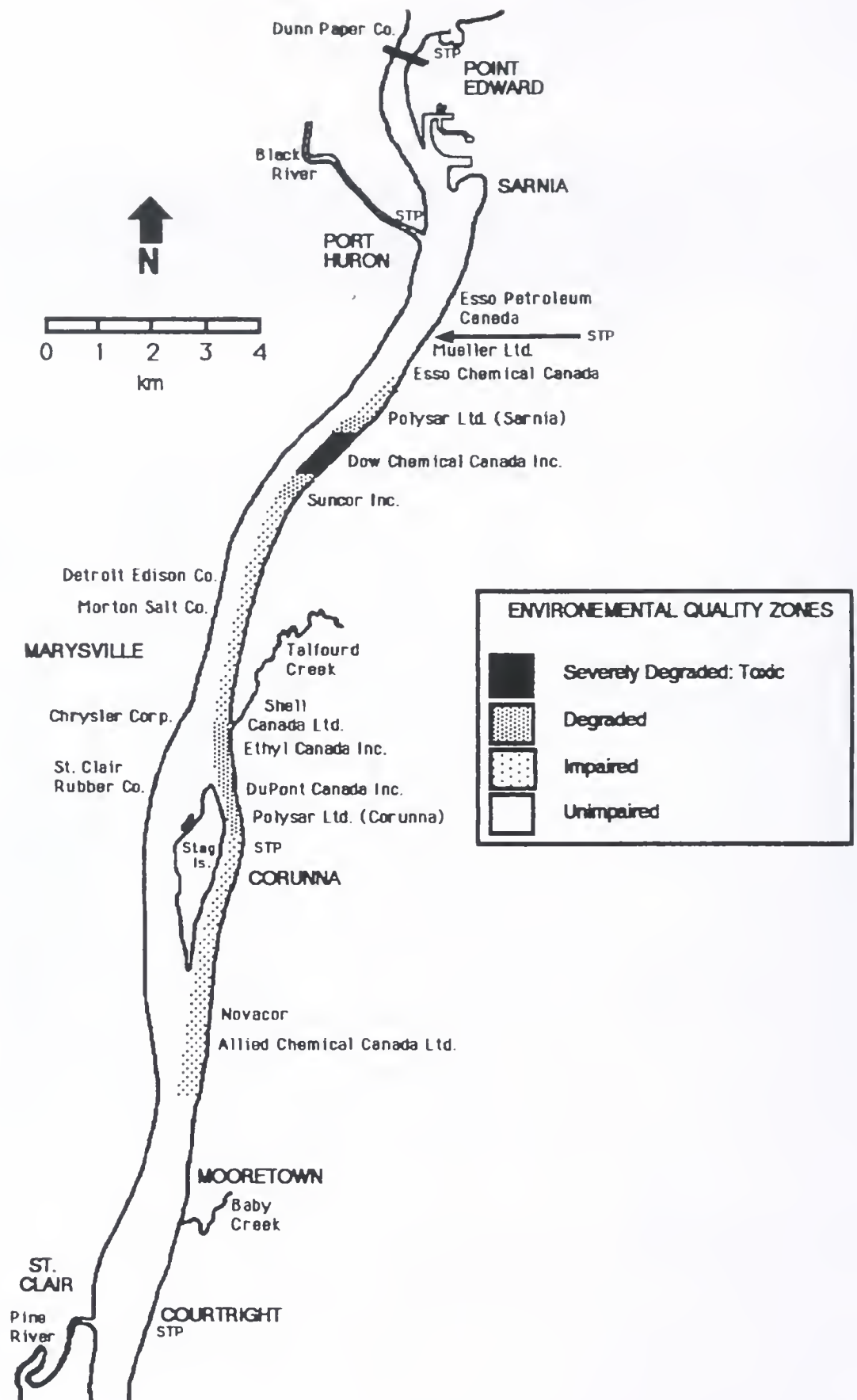


FIGURE 4.4.7: Environmental quality zones in the St. Clair River based on the distribution of benthic fauna (May 1985)

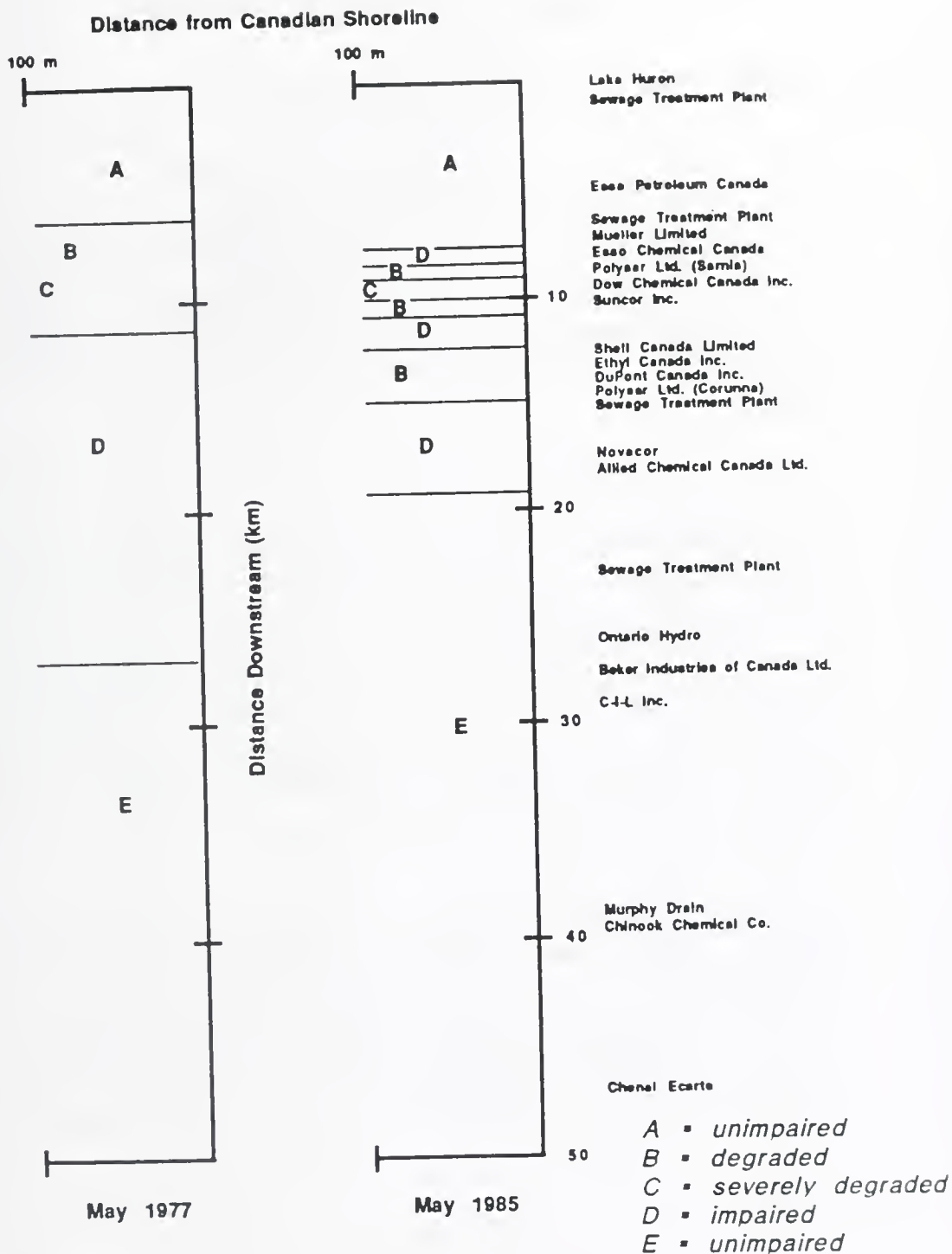


FIGURE 4.4.8: Distribution of environmental quality zones in the St. Clair River in the spring of 1977 and 1985

#### 4.4.7 In-Place Pollutants - Benthic Contaminant Residues

##### (a) Methods

Bottom water samples, surficial sediment samples, benthic invertebrates and sculpins were collected at up to 9 stations in the St. Clair River as outlined in Table 4.4.8 and Figure 4.4.9. All sediment samples were collected using a 23 cm X 23 cm Ponar grab sampler. The top 5 cm of sediment was sampled, refrigerated and returned to MOE laboratories in Rexdale for chemical analysis. Analytical methods are outlined in MOE (1981).

A separate set of sediment samples were sieved in the field through a U.S. #30 mesh wash bucket and the retained organisms sorted into taxonomic groups. Samples were submitted for taxonomic identification as outlined in Jaagumagi (1987). An evaluation of the benthic community is provided in Section 4.4.6. Benthic taxa which were collected in sufficient quantities for chemical analysis (5-10 gm wet wgt.) were blotted dry, wrapped in aluminum foil and frozen until analysis. Chemical analyses was performed as outlined in Ocean Chem (1988).

Sculpins were collected by diver, wrapped in aluminum foil and stored frozen. Sculpins were identified to species, aged and 2-4 fish composites of like-aged fish were submitted for chemical analysis using methods outlined by Ocean Chem (1988). Analytical results for metals, PCB/OC, chlorinated aromatics, and PAHs were obtained; however the following discussion focuses on HCE, HCB, HCB and OCS.

##### (b) Results

Although more detailed discussions of temporal and spatial trends observed for water and sediment quality data are given elsewhere in this report (see sections 4.2.2 and 4.3.1), it is pertinent to discuss the results obtained through coincident sampling, insofar as they relate to contaminant levels in benthos and sculpins.

TABLE 4.4.8: IN-PLACE POLLUTANTS SAMPLING LOCATIONS AND SAMPLE TYPES COLLECTED

STAT.	SAMPLE COLLECTED				
219	sediment	bottom water	benthic community structure	benthic	sculpins
110	sediment	bottom water	benthic community structure	benthic inverte.	--
203	sediment	bottom water	benthic community structure	--	--
218	sediment	bottom water	benthic community structure	benthic inverte.	--
38A	sediment	bottom water	benthic community structure	benthic inverte.	sculpins
64	sediment	bottom water	benthic community structure	benthic inverte.	sculpins
68	sediment	bottom water	benthic community structure	benthic inverte.	sculpins
34	sediment	bottom water	benthic community structure	benthic inverte.	sculpins
115	sediment	bottom water	benthic community structure	benthic inverte.	sculpins

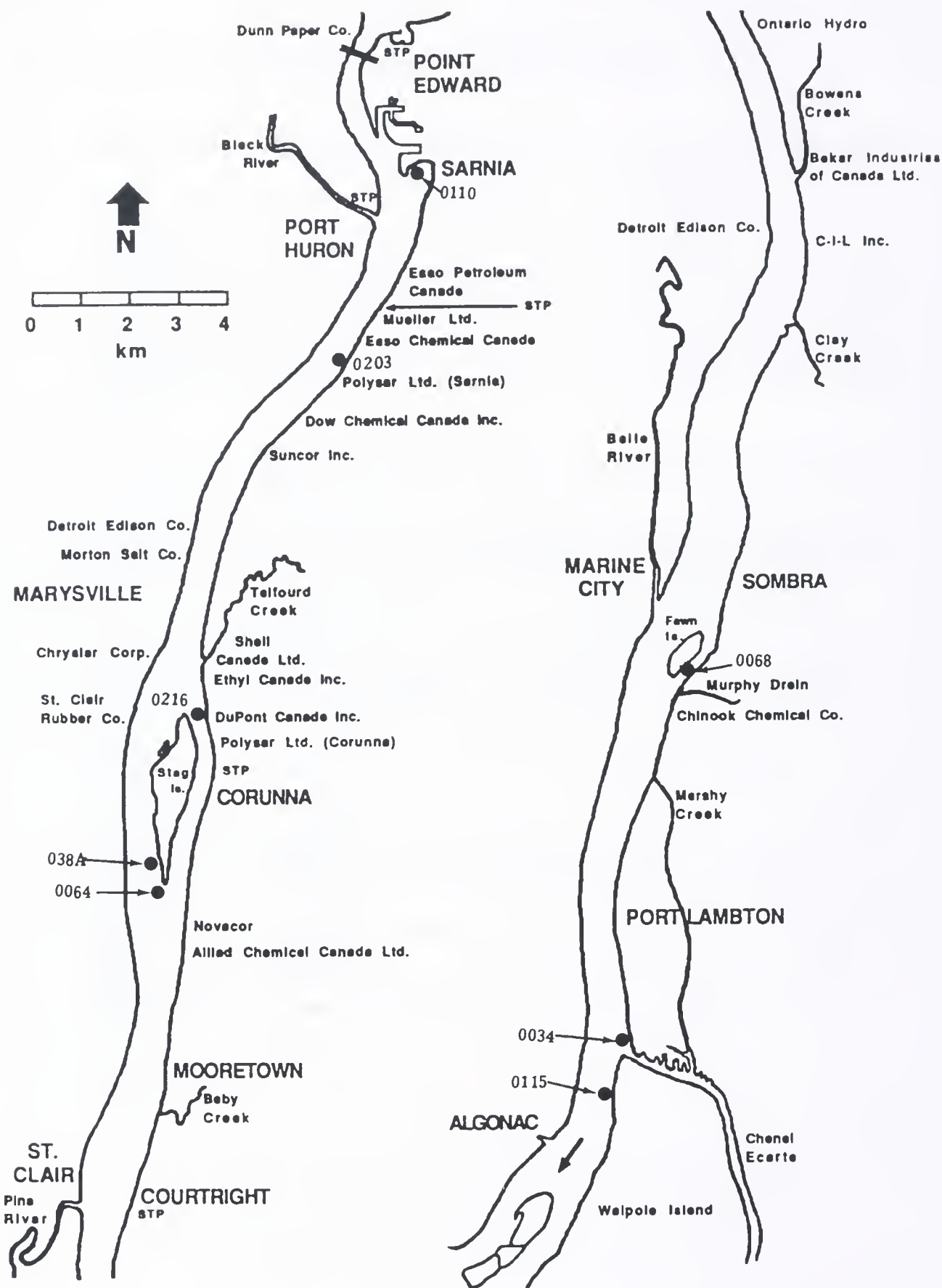


FIGURE 4.4.9: IN-PLACE POLLUTANTS SAMPLING LOCATIONS

It was not possible to collect sufficient biomass of one taxa of benthic invertebrate at all nine locations. Presence/absence of certain taxa was determined in part by physical factors such as sediment type, presence of macrophytes and current. Samples of the following benthos were submitted for chemical analysis: mayflies, amphipods, leeches, caddis fly larvae and chironomid larvae. However, as differences existed between contaminant levels in different taxa from the same site in some instances, spatial comparisons of contaminant residues were made using data from the same taxa. The taxa collected at most stations was the mayfly larvae, Hexagenia.

Levels of HCE in water, sediment and benthic biota were at or below the detection level at all locations.

Levels of HCB in water and sediment were at or below detection level at all but two stations (Table 4.4.9) near the mouth of the St. Clair River where bottom water concentrations were 13 ng/L and 3 ng/L. Detectable levels of HCB in Hexagenia were found in the St. Clair but no spatial trend was apparent, nor was there a relationship between sediment levels and levels in Hexagenia.

Levels of HCB in water were below detection at all sites (Table 4.4.10). In sediments, HCB concentrations were 2 ng/g upstream of the Sarnia complex, 108 ng/g downstream of Polysar, 350 ng/g downstream of Dow; declined with distance downriver then rose to peak again at 200 ng/g at Station 34. Concentrations of HCB in Hexagenia were positively correlated to levels in sediment (Figure 4.4.10) and followed a similar spatial pattern at the five stations tested in the lower river. In laboratory experiments with radiolabelled HCB, Bedard (unpublished) found that sediment was the principal source of HCB to Hexagenia.

Levels of OCS in water were below detection at all sites (Table 4.4.11). In sediment, levels of OCS were <1 ng/g upstream of the Sarnia complex and were at a maximum at Station 218 downstream of Dow. Elevated levels were also observed at Stations 68, 34 and 115 in the lower river. As with HCB, concentrations of OCS in Hexagenia were positively correlated to sediment OCS concentrations (Figure 4.4.11).

TABLE 4.4.9: CONCENTRATIONS OF HCB<sub>D</sub> IN BOTTOM WATER (ng/L), BULK SEDIMENT (ng/g DRY WT.), HEXAGENIA (ng/g WET WT.), AND SCULPIN (ng/g WET WT.)

STATION	WATER	SEDIMENT	<u>HEXAGENIA</u>	SCULPIN
control	-	-	-	5.0
219	<1	<1	-	-
110	<1	<1	-	-
203	<1	<1	-	-
218	<1	<1	-	-
38A	<1	<1	45.0	8.0
64	<1	<1	43.0	7.0
68	<1	<1	13.0	46.0
34	13	<1	5.0	-
115	3T	<1	33.0	-



TABLE 4.4.10: CONCENTRATIONS OF HCB IN BOTTOM WATER (ng/L), BULK SEDIMENT (ng/g DRY WT.), HEXAGENIA (ng/g WET WT.), AND SCULPIN (ng/g WET WT.)

STATION	WATER	SEDIMENT	<u>HEXAGENIA</u>	SCULPIN
control	-	-	-	3.0
219	<1	2.0	-	-
110	<1	3.0	-	-
203	<1	108.0	-	-
218	<1	350.0	-	-
38A	<1	2.0	12.0	3.0
64	<1	10.0	6.0	5.0
68	<1	64.0	45.0	18.0
34	2T	200.0	126.0	-
115	<1	31.0	20.0	-

FIGURE 4.4.10: Relationship between [HCB] in Sediments and [HCB] in Hexagenia

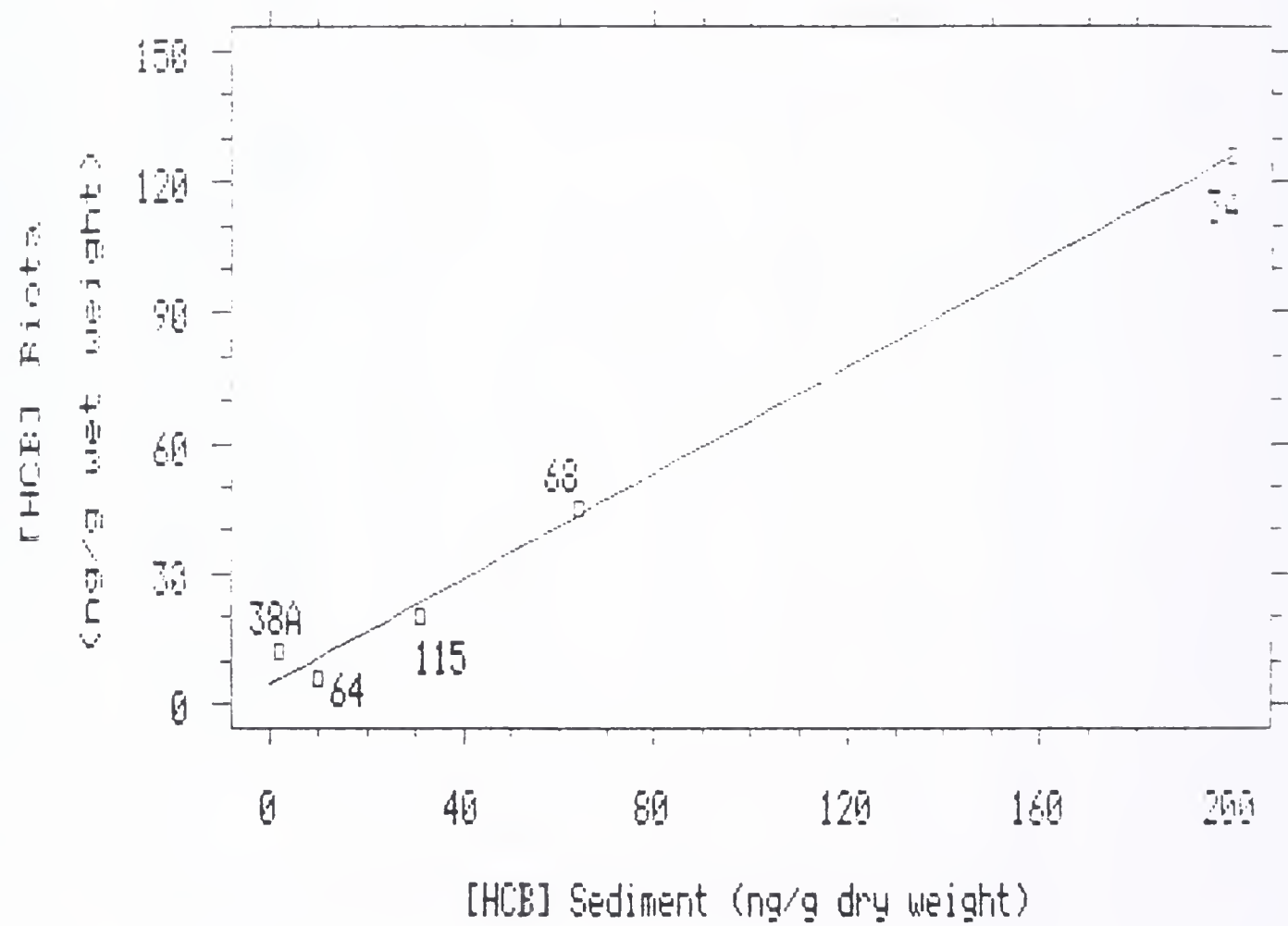
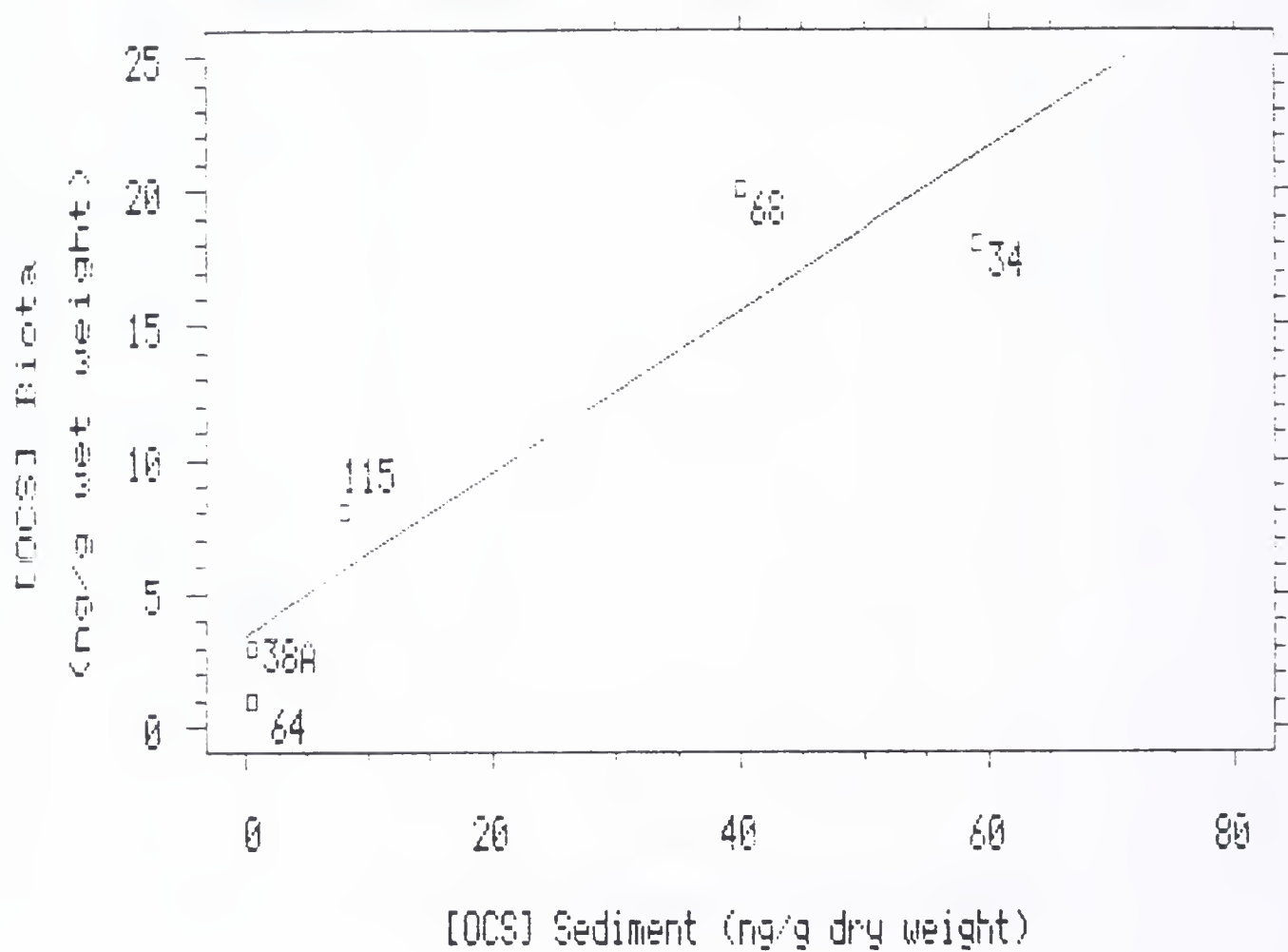


TABLE 4.4.11: CONCENTRATIONS OF OCS IN BOTTOM WATER (ng/L), BULK SEDIMENT (ng/g DRY WT.), HEXAGENIA (ng/g WET WT.), AND SCULPIN (ng/g WET WT.)

STATION	WATER	SEDIMENT	<u>HEXAGENIA</u>	SCULPIN
control	-	-	-	6.0
219	<1	<1	-	-
110	<1	<1	-	-
203	<1	<1	-	-
218	<1	54.0	-	-
38A	<1	<1	3.0	2.0
64	<1	<1	<2.0	8.0
68	<1	40.0	20.0	40.0
34	<1	59.0	18.0	-
115	<1	8.0	8.0	-

FIGURE 4.4.11: Relationship between [OCS] in Sediments and [OCS] in *Hexagenia*



Concentrations of HCBD, HCB and OCS in sculpins collected at Station 68 were elevated above the levels found in sculpins collected upstream of the Sarnia industrial complex.

#### 4.4.8 Caged Clams

##### (a) Purpose

A biomonitoring study using caged clams was conducted in order achieve several goals:

- i) To complement and update similar studies conducted on the St. Clair River during 1982-1983;
- ii) To identify and quantify those compounds which are bioavailable and may tend to concentrate;
- iii) To develop a simple and effective method for sample preparation for volatiles analysis.

##### (b) Introduction and Methods

Clams were collected from Balsam Lake near Rosedale, Ontario (Lat. 44° 34' 45" N, Long. 78°48'05"W) June 11, 1986. This lake supports healthy clam and fish primarily for recreational purposes. Divers retrieved clams from within a several hundred square meter area in Balsam Lake in approximately 2m of water. Clams ranging in maximum shell length from 6.5 cm to 7.2 cm were selected and transported in clean polyethylene bags of Balsam Lake water. Sufficient clams were collected to deploy at eleven ecosystem stations (Figure 4.4.12). Stations at the head and mouth of the St. Clair River had clams deployed at mid-depth only. For stations situated along the river length clams were deployed at mid-depth and on the bottom.

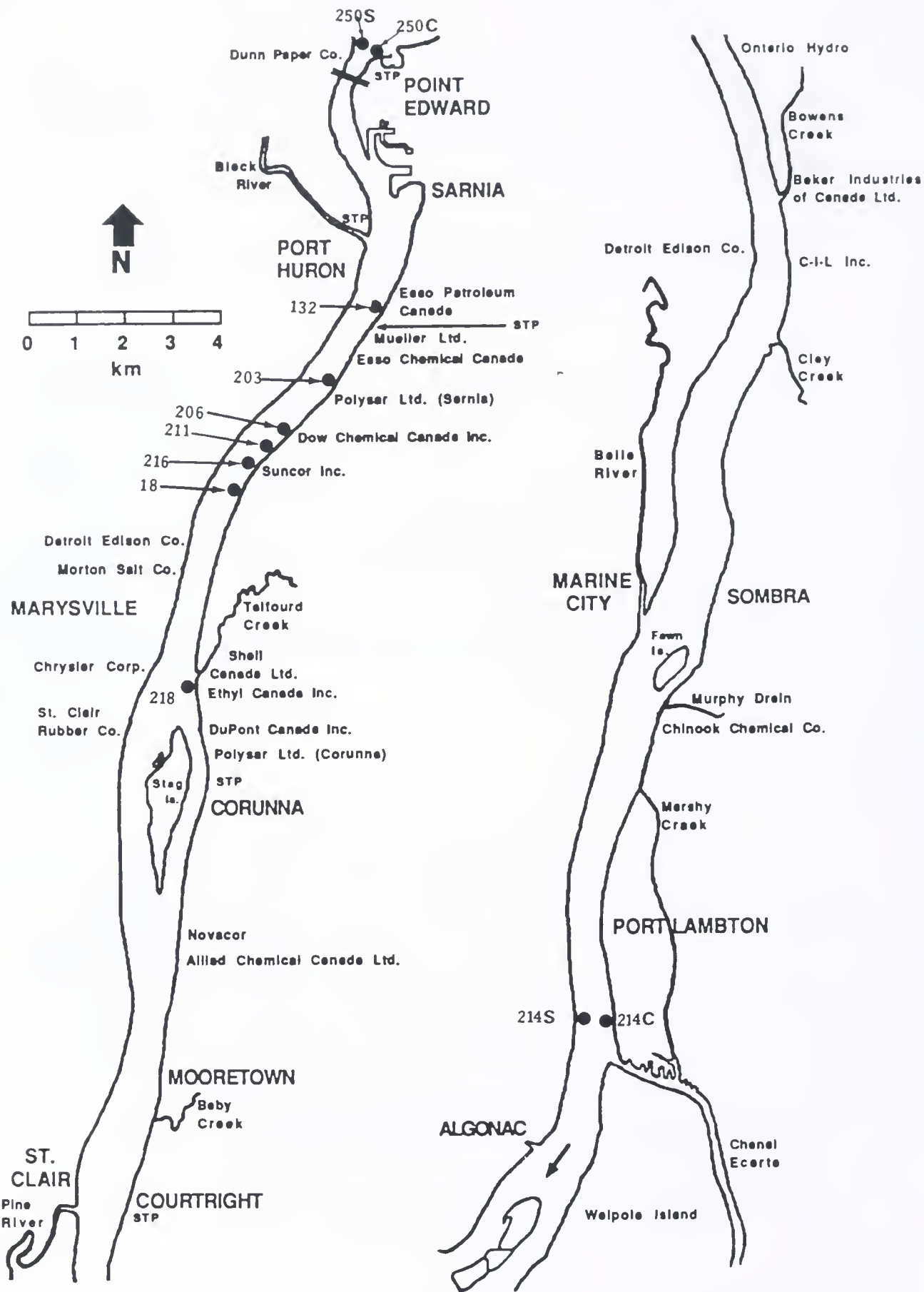


FIGURE 4.4.12: CAGED CLAM SAMPLING STATIONS

At each monitoring station, one or two galvanized steel mesh cages containing clams were anchored to the bottom by means of lead anchoring weights and where possible tethered with fine stainless steel cable to some easily recognized shoreline structure. Where two cages were deployed, one contained a float so that the cage was suspended approximately at mid-depth. Water depths at stations varied from 1m to 12m. Photographs and shore references were utilized to locate stations for future visits.

Clams were deployed in the St. Clair River on June 13-14th, 1986 within 72 hours after their collection from Balsam Lake. The first recovery was 31 days later on July 15th and 16th, 1986. The second recovery was on October 26th, 1986, 134 days after deployment. In cases where cages could not readily be located for retrieval, SCUBA divers attempted to do so.

Upon retrieval all clams were immediately put on ice. Within 24 hours, clams were shucked, wrapped in hexane rinsed foil, and frozen. Clam ages were determined by counting the growth lines in the shells. Tissue wet weight was recorded prior to submission for analysis.

At each station, measurements were made of temperature, conductivity, dissolved oxygen, pH, and flow rate during deployment and recovery.

Concurrent with deployment and retrieval and at approximately monthly intervals during this time, mid-depth and bottom water samples were obtained. These samples were analysed for volatiles, organochlorine contaminants and water chemistry (Table 4.1.1) with the exception of major ions.

Tissue from 10 clams were prepared and submitted the same day for analysis for volatile and chlorinated aromatic compounds (Table 4.4.12). Of the twelve clams per cage exposed in the St. Clair River, three were analysed for volatiles and a further three analysed



TABLE 4.4.12: CLAM TISSUE PARAMETER LIST

<u>Volatile Organic Compounds:</u>	<u>Chlorinated Aromatic Compounds:</u>
<p>Methylene Chloride</p> <p>1,1-Dichloroethylene</p> <p>Bromochloromethane</p> <p>1,1-Dichloroethane</p> <p>Chloroform</p> <p>1,2,-Dichloroethane</p> <p>1,1,1-Trichloroethane</p> <p>Carbontetrachloride</p> <p>Dichlorobromomethane</p> <p>1,2-Dichloropropane</p> <p>Benzene</p> <p>Trichloroethylene</p> <p>1,1,2-Trichloroethane</p> <p>Chlorodibromomethane</p> <p>1,2-Dibromoethane</p> <p>Bromoform</p> <p>1,3-Dichlorobutane</p> <p>Tetrachloroethylene</p> <p>Toluene</p> <p>1,1,2,2-Tetrachloroethane</p> <p>Chlorobenzene</p> <p>Ethylbenzene</p> <p>m-Xylene</p> <p>o- or p-Xylene</p> <p>1,2-Dichlorobenzene</p> <p>Detection limit: 10 ng per sample (dependent upon sample size)</p>	<p>Hexachloroethane</p> <p>1,3,5-Trichlorobenzene</p> <p>1,2,4 Trichlorobenzene</p> <p>Hexachlorobutadiene</p> <p>1,2,3-Trichlorobenzene</p> <p>2,4,5-Trichlorotoluene</p> <p>2,3,6-Trichlorotoluene</p> <p>1,2,3,5 Tetrachlorobenzene</p> <p>1,2,4,5 Tetrachlorobenzene</p> <p>2,6,a-Trichlorotoluene</p> <p>1,2,3,4 Tetrachlorobenzene</p> <p>Pentachlorobenzene</p> <p>Hexachlorobenzene</p> <p>Octachlorostyrene</p> <p>Detection limit: 1 ng/g (1 ppb)</p>

for chlorinated aromatic hydrocarbons. Exposure times were for 4 or 15-19 weeks with an equal number of clams analysed from each retrieval.

Clams submitted for analysis of chlorinated aromatic hydrocarbons were subject to acid digestion followed by solvent extraction and analysis by gas chromatography.

(i) Clam Tissue Preparation for Volatiles Analysis

The measurement of volatile organic compounds in media other than surface water and effluent has not advanced to a routine stage, and protocols are still under development.

The nature of these compounds is such that special care must be taken to avoid excessive losses to the atmosphere due to volatilization. Conversely, ambient volatiles may be introduced to samples which remain in storage prior to analysis.

To minimize problems incurred in clam tissue preparation, a method was developed using liquid nitrogen to freeze the tissue and a system to pulverize the frozen mass. This method is discussed in further detail in Appendix 6a.

(c) Results and Discussion

The highly energetic environment of the St. Clair River poses some significant difficulties to any type of study of this variety. Swift currents coupled with intensive commercial and sporting uses provide ample opportunity for accidents and/or tampering to occur.

Several problems were encountered with respect to a low incidence of cage recovery. Following the initial 4 week exposure period, approximately 60% of deployed cages were recovered. This percentage dropped to 20% following the additional 15 week exposure period. This

latter figure is unacceptable in terms of enabling a suitable assessment. It certainly precludes a statistical comparison and weakens any qualitative assessment.

Reasons for low recovery can only be postulated and may include tampering, unintentional contact with cages or tethering, or in some cases, physical perturbation from currents and/or propeller wash.

A similar study by Kauss and Hamdy (1985) in the St. Clair and Detroit Rivers had significantly better recovery than achieved during this study. Clams were deployed in shallower water (1-4 m) than during 1986 ( $\bar{x} = 5.2$  m) and closer to shore (1-50 m) than in 1986 (15-135 m). These two factors may have contributed to improved recovery.

Table 4.4.13 indicates the results of clam retrieval after four and 15 - 19 weeks. Following four weeks exposure, seven of eleven stations were recovered in varying degrees of completeness. In some instances, only mid-depth cages were recovered, while bottom cages could not be located. In one instance (Station 216) some obvious tampering appeared to have occurred as a stainless steel coupling had been unfastened, and the wire cast off. In this instance, the clams were recovered following a lengthy search by divers.

Recovery during the second phase was limited to three of ten stations. Again, evidence of tampering was observed at Station 216; however, the cages were not located on this attempt.

Cage recovery is dependent upon several factors, particularly in a river environment. Current velocity in the St. Clair River varies considerably, and increases with increasing distance from shore. Drogue tracking studies conducted by the U.S. Army Corps of Engineers in 1982 revealed current velocities ranging from 0.6 m/s to 2.0 m/s in mid-river.

TABLE 4.4.13: CLAM RETRIEVALS AND OBSERVATIONS

RECOVERY I (4 weeks)		RECOVERY II (15*-19 weeks)
STATION	COMMENTS	COMMENTS
25 US	<ul style="list-style-type: none"> <li>- Cages not located</li> <li>- New cages not deployed</li> </ul>	<ul style="list-style-type: none"> <li>- Cages were not deployed following recovery I</li> </ul>
25 CAN	<ul style="list-style-type: none"> <li>- Cages not located</li> <li>- New cages deployed (2 depths; 16 clams/cage)</li> </ul>	<ul style="list-style-type: none"> <li>- Cages not located</li> </ul>
132	<ul style="list-style-type: none"> <li>- Successful recovery</li> </ul>	<ul style="list-style-type: none"> <li>- Wire broken; cages not located</li> </ul>
203	<ul style="list-style-type: none"> <li>- Cages not recovered</li> <li>- New cages deployed (2 depths; 17 clams/cage)</li> </ul>	<ul style="list-style-type: none"> <li>- Cages not recovered</li> </ul>
206	<ul style="list-style-type: none"> <li>- Successful recovery</li> </ul>	<ul style="list-style-type: none"> <li>- Line not found</li> </ul>
211	<ul style="list-style-type: none"> <li>- Successful recovery</li> </ul>	<ul style="list-style-type: none"> <li>- Line broken; cages not located</li> </ul>
216	<ul style="list-style-type: none"> <li>- Line found unfastened; clams recovered and reattached; 1 clam dead in bottom cage</li> </ul>	<ul style="list-style-type: none"> <li>- Line found unfastened</li> </ul>
18	<ul style="list-style-type: none"> <li>- Bottom cage recovered with 11 clams (1 dead); new cages deployed (12 in mid; 17 in bottom cage)</li> </ul>	<ul style="list-style-type: none"> <li>- *Mid-depth cage located; 3 clams dead</li> </ul>
218	<ul style="list-style-type: none"> <li>- Cages not recovered;</li> <li>- New cage deployed; (20 in bottom cage)</li> </ul>	<ul style="list-style-type: none"> <li>- *Bottom cage recovered; 1 clam dead</li> </ul>
214 CAN	<ul style="list-style-type: none"> <li>- Successful recovery</li> </ul>	<ul style="list-style-type: none"> <li>- Successful recovery</li> </ul>
214 US	<ul style="list-style-type: none"> <li>- Successful recovery</li> </ul>	<ul style="list-style-type: none"> <li>- Line broken, cages not located</li> </ul>

TABLE 4.4.14: 1986 MISA CLAM EXPOSURE STATIONS: LOCATION AND PHYSICAL CHARACTERISTICS

STN. #	LOCATION	DIST. FROM SHORE		WATER DEPTH (m)	CURRENT (cm/s)			SUBSTRATE
		CAN	U.S.		BOTTOM	MID	SURFACE	
25 CAN	SR 39.0 - Sarnia Yacht Club	30	400	3	66	-	41	Concrete blocks, rock, sand
25 US	SR 39.0 US - near lighthouse	-	15	-	-	-	72	Small rock
132	Imperial Oil dock	30	-	8	54	45	49	Small rock, clay
203	Cole Drain outfall - at submerged end of pipe	68	-	12	44	91	107	Clay
206	600 ft. downstream of Dow 1st St. complex	15	-	7	21	49	74	Clay, small rocks
211	Adjacent to Dow; downstream of 3rd St. sewer	15	-	4	34	-	40	Clay, small rocks
216	SR 33.8 - downstream of Dow 4th St. sewer	15	-	5	41	45	59	Clay, small rocks, weeds
18	SR 33.4 - downstream of Suncor ramp	15	-	5	15	11	16	Silty, weeds
218	Downstream - Talfourd Creek	45	-	1	5	-	6	Weeds, silt, small rocks
214 CAN	SR 12.9 - upstream from Chenal Ecarte	135	-	2	9	-	13	Weeds, silt, small rocks
214 US	SR 12.9	-	45	5	13	-	64	Weeds, silt, small rocks
x		41	153	5.2	30.2	48.2	49.8	

Velocity has been demonstrated to reduce logarithmically with increasing depth (Derecki and Quinn 1987) and would therefore be lower near the bottom cage. The mean depth of bottom cages was 5.2m.

Clams were situated at distances from 15 to 135m from shore (Table 4.4.14) where current velocity was typically on the order of 0.5 m/s at the surface, decreasing to 0.3 m/s at the river bottom (Table 4.4.14). This reflects the normal pattern of increasing friction and reduced velocity approaching the shore in a river environment (Fischer et al. 1979); however, the velocity is sufficient in most cases to dislodge cages in the event that a line is broken. This conclusion has been verified by diver observation.

Other factors contributing to the loss of cages include commercial and sport vessels which may interfere with lines and/or cages. Affixing cages to shore or an immovable object is desirable; however, this increases visibility and the likelihood of contact from boaters and/or individuals on shore.

A method whereby cages are affixed to heavy weights with limited visibility may offer a more suitable alternative. The potential for a remotely operated surfacing buoy has been considered, as this will eliminate contact with shore, and minimize visibility until the buoy is triggered to surface for retrieval. A serious drawback to this method is the cost to purchase equipment and the potential for loss. Unless a more suitable method can be developed, this latter option should be considered.

An abbreviated list of compounds detected in clam tissues is presented in Table 4.4.15. Selection of compounds was based upon documented sources in the area as well as the potential for detrimental effects to the ecosystem. Detailed results for selected parameters are presented in Appendix 6b.

A previous and more comprehensive investigation by Kauss and Hamdy (1985) using clams in the St. Clair and Detroit Rivers revealed that wet



weights and lipid contents did not change appreciably during a three week exposure. As such, no normalization of data to standard weights or lipid levels was undertaken from 1986 results.

Clams exposed for 15-19 weeks did not appear to undergo any weight reduction during this study. In fact, mean wet weights at similar stations, were higher than for clams exposed for four weeks.

The investigation by Kauss and Hamdy (1985) using clams in the St. Clair and Detroit Rivers revealed that wet weights and lipid contents did not change appreciably during a three week exposure. As such, no normalization of data to standard weights or lipid levels was undertaken from 1986 results.

Clams exposed for 15-19 weeks did not appear to undergo any weight reduction during this study. In fact, mean wet weights at similar stations, were higher than for clams exposed for four weeks.

The distribution of organic contaminants is highlighted in Table 4.4.16 and Figures 4.4.13 to 4.4.15. As anticipated, uptake levels were highest downstream of the "Chemical Valley" complex, particularly in the vicinity of Dow Chemical and at the southern boundary of Suncor.

Hexachlorobenzene levels (Figure 4.4.13) were highest at Station 206 following a four week exposure; however, clams could not be located during the 2nd attempted recovery. Values observed at Station 18 following nineteen weeks exposure were somewhat higher than tissue concentrations following 4 weeks exposure. This may indicate that uptake/depuration rates had not achieved steady state at Station 18 after four weeks, as body burdens peaked sometime after this time. Alternatively, clams exposed for nineteen weeks may reflect degraded conditions during the latter portion of their exposure. Muncaster (1987) suggests that a much briefer period is required to achieve steady state.



**TABLE 4.4.15: MEAN CLAM TISSUE CONCENTRATIONS FOR SELECTED CONTAMINANTS (ng/g)**

STATION	HCB	HCBd	HCE	OCS	BENZENE	PERC.	ET. BENZ.
132 mid.	0/-	0/-	0/-	-	-/-	-/-	-/-
132 bot.	0/-	0/-	0/-	-	9.6(2)/-	0(2)/-	128(2)/-
206 mid.	35/-	56/-	0/-	-	-/-	-/-	-/-
206 bot.	33/-	49/-	0/-	-	12.8(2)/-	5.5(2)/-	33(2)/-
211 mid.	10/-	20/-	0/-	-	-/-	-/-	-/-
211 bot.	19/-	69/-	0/-	-	-/-	-/-	-/-
216 mid.	9/-	15/-	0/-	-	-/-	-/-	-/-
216 bot.	21/-	21/-	0/-	-	11.2(2)/-	16.6(2)/-	33.5(2)-
18 mid.	-/14	-/3	-/0	-/32	-/-	-/-	-/-
18 bot.	19/33	151/0	0/0	-/33	4.2(2)/10.8(3)	6(2)/4.2(3)	10(2)/0(3)
218 bot.	-/11*	-/4*	-/0*	-/22*	-/13(2)*	-/0(2)*	-/0(2)*
214C mid.	4/-	4/-	-	-	-/-	-/-	-/-
214C bot.	3/10(6)	3/0(6)	-	-	-/10(1)	-/0(1)	-/0(1)
214V mid.	0/-	0/-	-	-	-/-	-/-	-/-
214V bot.	0/-	0/-	-	-	-/-	-/-	-/-
Balsam Lake	0(5)	0(5)	0(5)	0(5)	-	-	-

Exposure periods: 4 weeks/19 weeks

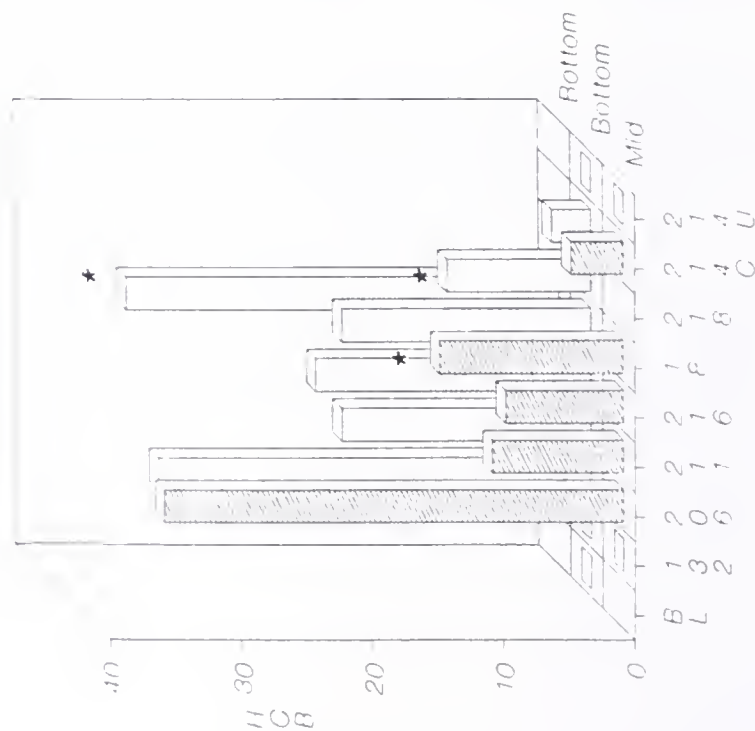
\* 15 weeks

- = not measured

n = 3 unless otherwise indicated in brackets

FIGURE 4.4.13

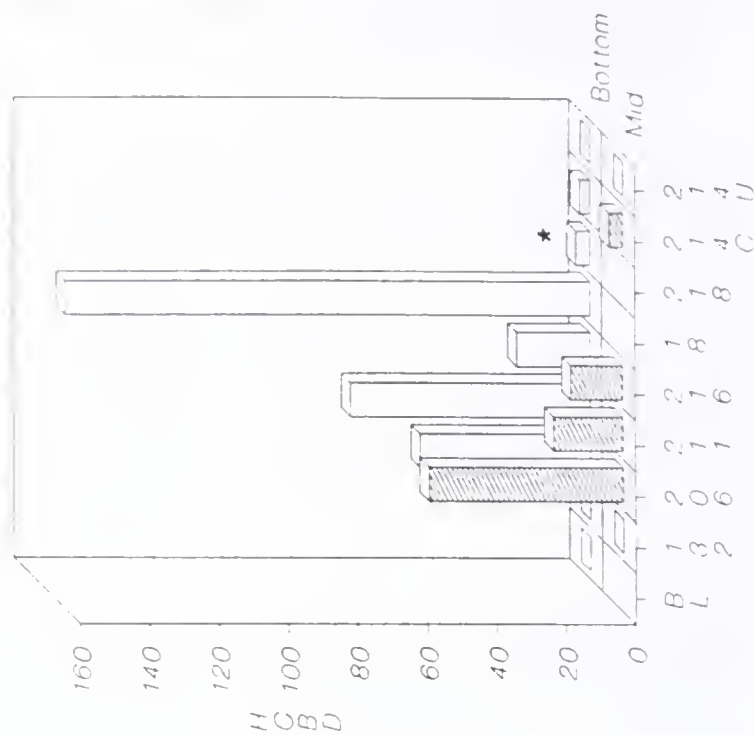
ST. CLAIR RIVER MISA CLAM STUDY  
 HEXACHLOROBENZENE (ng/g)



STATION

Exposure: ★ 15 weeks

HEXACHLOROBUTADIENE (ng/g)



STATION

HCB concentrations in clams exposed in bottom cages were occasionally elevated over mid-water exposure. This likely reflects availability by means of resuspended fine materials which are ingested by clams. This is corroborated by elevated suspended solids levels in bottom waters, particularly at Stations 211 and 218 which were 1 and 1.5 times higher than in surface waters during sampling in August 1986. Concurrent HCB levels in whole water revealed an even more pronounced vertical gradient as bottom versus top water grabs at Station 218 contained 190 and 2 ng/L HCB respectively. Additional water data has been discussed as part of the "Investigative" portion of this document (Section 4.2.2).

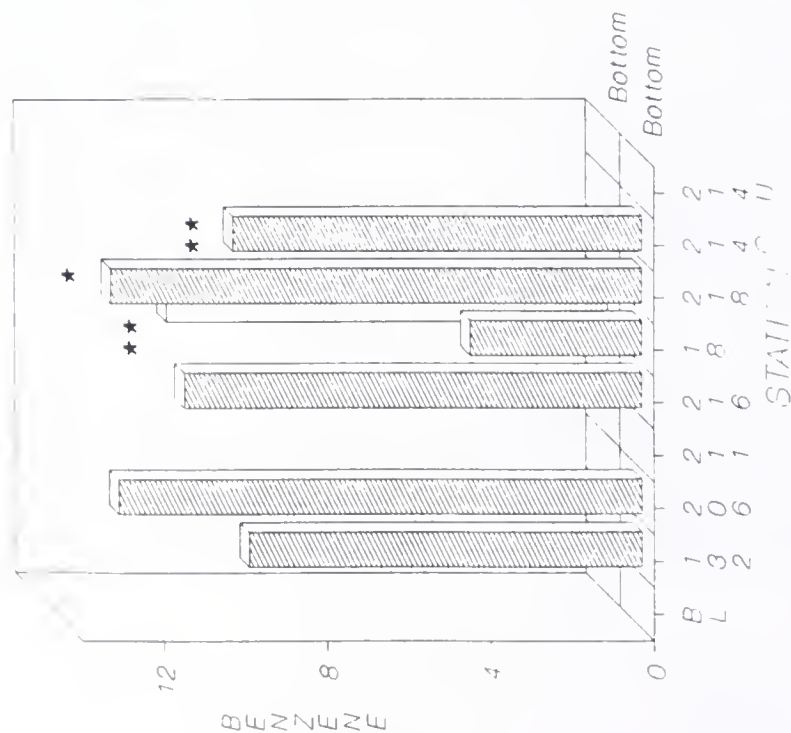
A somewhat stepwise reduction in HCB levels was observed with increasing distance downstream reflecting a gradual improvement of conditions; however, lethality did not occur until downstream of sources and not in the immediate vicinity at sources as might be expected (Table 4.4.13). Only one clam died at each of stations 216 and 218 while three were found dead at Station 18. This latter number represents approximately 16% mortality and is higher than expected for background or natural mortality.

Levels of HCBd followed a roughly similar pattern to HCB; however elevated levels were observed at Station 211 downstream of the Dow 3rd St. sewer. The highest level (151 ng/g) was measured at Station 18 along the bottom after only 4 weeks exposure. No concomitant clam was available from mid-depth at this station. Again, a fairly rapid drop off was noted downstream of Station 18; however, measurable levels were recorded in tissue collected from as far downstream as Chenal Ecarte.

Fish flesh criteria established by the New York State Dept. of Environmental Conservation, for the protection of fish-eating wildlife were not exceeded except for octachlorostyrene. Criteria for HCB, HCBd, HCE and OCS are 330, 1300, 14100, and 20 ng/g respectively.

FIGURE 4.4 14

ST. CLAIR RIVER MISA CLAM STUDY  
BENZENE (ng/g)



Exposure \* 15 weeks \*\* 19 weeks

ST. CLAIR RIVER MISA CLAM STUDY  
ETHYLBENZENE (ng/g)

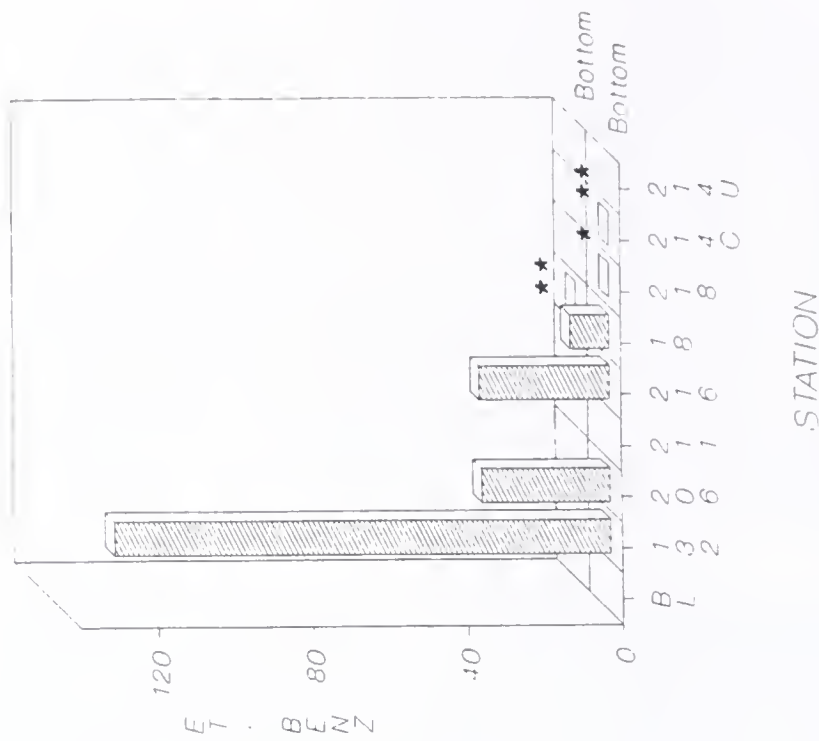
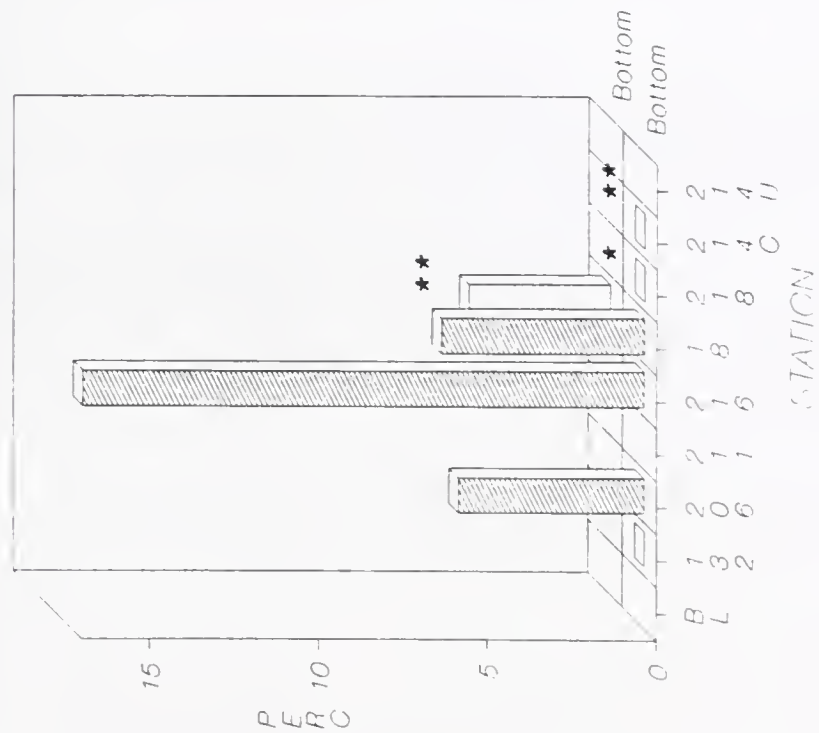


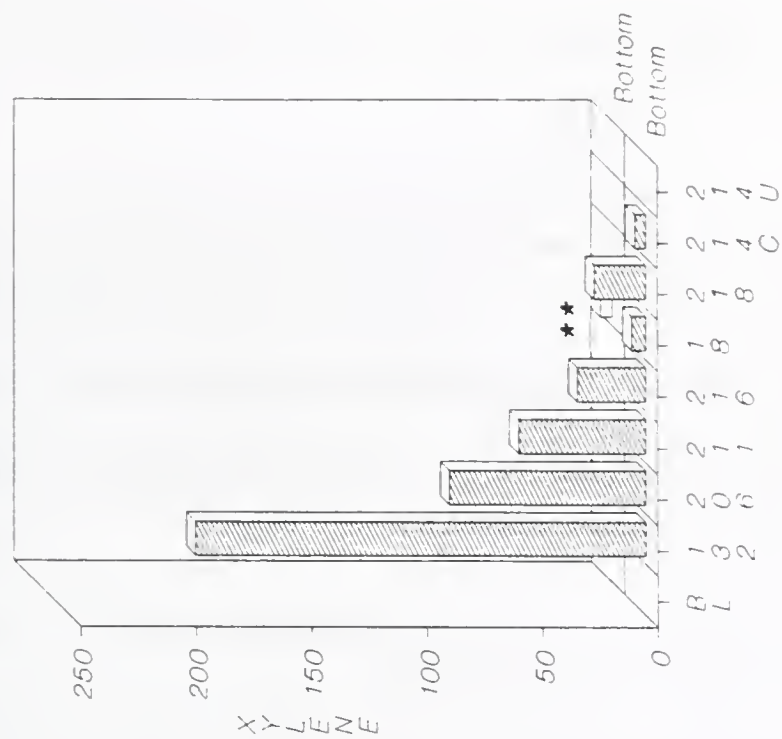
FIGURE 4.4.15<sup>1</sup>

ST. CLAIR RIVER MISA CLAM STUDY  
PERCHLOROETHYLENE (ng/g)



Exposure: \* 15 weeks \*\* 19 weeks

ST. CLAIR RIVER MISA CLAM STUDY  
m-o-,p-XYLENE (ng/g)



Several volatile compounds were repeatedly measured in clam tissues. These included benzene, chloroform, ethylbenzene and xylene (Figures 4.4.14 to 4.4.15).

The methods for determination of volatile organic compounds in biological tissue and sediments are under development and levels should be considered estimates of minimum values. Currently there are several significant assumptions which may effect quantitative determination for either of these media. These assumptions are as follows:

1. The purging efficiency of the compound is identical to that of the internal standard added to each sample.
2. The GC (gas chromatograph) behaviour of the compound is identical to that of the internal standard.
3. The MS (mass spectrometer) response of the compound is identical to that of the internal standard.

Until a validated method has been developed; results are to be viewed as minimum values; however, values which are presented, enable a relative comparison and as such are useful for identifying areas of point source contamination.

Xylene concentrations were reduced in a step-wise fashion from peak values measured at Station 132. This likely reflect inputs from Esso Chemical, a producer of  $22 \times 10^3$  tonnes/year xylene (Corpus 1983).

Ethylbenzene, which is produced primarily at Polysar in the manufacture of styrene with some production at Dow (Corpus, 1981) had peak concentrations at the Cole drain and again downstream of the Dow 4th St. outfall.

Perchloroethylene (PERC), manufactured at Dow Chemical and used as a drycleaning and metal degreasing solvent was highest downstream of the Dow 4th St. Sewer.

Benzene concentrations were generally low (8-12 ppb) and widely distributed. Sources in the "Chemical Valley" include Esso Chemical, Polysar and Suncor (Corpus 1982).

Data from MISA point source monitoring demonstrates a cause effect relationship for several compounds including HCB, HCBd and PERC with elevated effluent concentrations resulting in corresponding peaks in tissue levels.

The usefulness of bioindicators such as clams is evident in that compounds such as xylene, benzene and ethylbenzene have no significant sources based on effluent monitoring. This may be due in part to method detection levels of these latter compounds up to 1000 times higher than the chlorinated aromatic compounds such as HCB and HCBd.

Accumulation studies using Elliptio complanata (Muncaster et al. 1987) have demonstrated rapid intake of compounds such as HCB and OSC with peak concentrations in 2-3 weeks and 3-9 weeks respectively.

This suggests that elevated levels observed following 15-19 week exposure periods may reflect environmental conditions for a much shorter period of time prior to retrieval. In this regard, it is probably not advisable to compare results for clams exposed at varying intervals as levels may reflect different degrees of uptake and depuration depending on water quality.

(d) Conclusions and Recommendations

- (i) Introduced clams are useful indicators of contaminant inputs which in some cases may not be detected in effluent or water samples.



- (ii) Clam tissue analysis identifies those contaminants which are bioavailable.
- (iii) Residue levels may reflect conditions for days to weeks immediately prior to sampling for those contaminants which achieve rapid equilibrium. This may not be the case for compounds such as HCB and OCS.
- (iv) Clam mortalities may provide indications of spills or other "upsets" during exposure, so long as exposed mortality is significant with respect to control mortality.
- (v) The preparation of clam tissue and subsequent analysis for volatile organic compounds requires refinement and development of a valid protocol.
- (vi) Clam exposure is a sensitive test of both horizontal and vertical contaminant gradients, as indicated by bottom vs. mid-depth and spatial results.

#### 4.4.9 Juvenile Fish

##### (a) Introduction and Methods

Young-of-the-year spottail shiners (Notropis hudsonius) and emerald shiners (Notropis atherinoides) were collected from a number of sites upstream and downstream of the Sarnia industrial complex (Figure 4.4.16). Individual fish were measured (total length), wrapped in hexane-rinsed aluminum foil and placed in plastic bags. Samples were stored in a frozen state at -20°C until analyzed.

Composite samples of ten fish each were homogenized and analyzed for contaminant residues at the Ontario Ministry of the Environment Laboratory in Rexdale. Packed column gas chromatography (GC) was used for hexachlorobenzene, octachlorostyrene, hexachlorobutadiene and

FIGURE 4.4.16 JUVENILE FISH COLLECTION SITES  
IN THE ST. CLAIR RIVER AND LAKES  
HURON AND ST. CLAIR



TABLE 4.4.16: CHLORINATED ORGANIC RESIDUES IN YOUNG-OF-THE-YEAR SPOTTAIL SHINERS FROM THE ST. CLAIR RIVER, LAKE ST. CLAIR AND LAKE HURON (VALUES IN NG/G, MEANS WITH SD, WET WEIGHT)

Sampling Site	Year	N	Fish Size (mm)	% Lipid	HCB	OCS	HCBD	HCE
1. Port Huron, Michigan	1986	5	50 ± 7	6.0 ± 7	3 ± 1	4 ± 2	ND	ND
2. Suncor	1983	4	46 ± 7	2.8 ± .3	231 ± 26	560 ± 148	NA	NA
3. Lambton Generating Stn.	1985	5	62 ± 4	3.4 ± .4	60 ± 13	81 ± 22	NA	NA
	1986	5	55 ± 4	2.8 ± .6	31 ± 13	104 ± 46	36 ± 6	ND
	1987	7	66 ± 4	5.0 ± .7	13 ± 2	35 ± 3	NA	NA
4. South Channel	1982	7	59 ± 7	2.0 ± .3	13 ± 7	95 ± 10	NA	NA
	1986	6	52 ± 6	2.0 ± .3	12 ± 2	49 ± 9	ND	ND
5. Chenal Ecarté	1983	7	57 ± 4	1.5 ± .1	10 ± 3	28 ± 8	NA	NA
	1987	7	53 ± 4	1.6 ± .2	6 ± 1	18 ± 6	ND	ND
6. Mitchell Bay	1978	8	54 ± 3	1.8 ± .2	ND	NA	NA	NA
	1979	7	55 ± 5	1.0 ± .2	ND	NA	NA	NA
	1982	7	58 ± 5	2.2 ± .2	1 ± 0	2 ± 0	NA	NA
	1984	7	58 ± 6	2.4 ± .4	ND	ND	NA	NA
	1985	6	61 ± 5	3.4 ± .8	10 ± 3	13 ± 4	NA	NA
	1986	7	57 ± 5	1.4 ± .1	2 ± 2	2 ± 1	ND	ND
	1987	7	58 ± 4	1.8 ± .1	2 ± 1	4 ± 2	ND	ND
DETECTION LIMITS					1	1	1	1
NA - Not analyzed ND - Not detected								

TABLE 4.4.17: VOLATILE HYDROCARBON RESIDUES IN YOUNG-OF-THE-YEAR  
EMERALD SHINERS FROM THE ST. CLAIR RIVER (ng/g wet wt.)

SAMPLING SITE	YEAR	N	Tetrachloro- ethylene	Carbon Tetrachloride
Point Edward	1986	1	TR	ND
Below Suncor	1985	1	380	ND
	1986	1	31	4
Lambton Gen. Stn.	1985	1	220	ND
	1986	1	12	ND
Port Lambton	1985	1	320	ND
	1986	1	4	ND
South Channel	1986	1	ND	ND

TR - trace

ND - not detected

hexachloro-ethane quantification, whereas purge and trap technique with GC/MS was used for tetrachloroethylene and carbon-tetrachloride residues.

(b) Results and Discussion

The levels of selected contaminants in juvenile fish are given in Tables 4.4.16 and 4.4.17.

For HCB, OCS, HCBd and HCE, spatial comparisons were made using data for spottail shiners collected in 1986. For tetrachloroethylene and carbon tetrachloride, comparisons were made using data for emerald shiners collected in 1985 and 1986.

(i) Temporal and Spatial Trends

Clear trends were apparent for HCB and OCS with levels at the control location (Port Huron, Michigan) being just above the detection limit and elevated levels occurring at the Sunoco and Lambton Generating Station (Figures 4.4.17 and 4.4.18). HCB and OCS concentrations were somewhat lower at the South Channel station and had returned to control levels at the Mitchell Bay station. The pattern of HCBd accumulation was similar. A similar spatial pattern of HCB and OCS in juvenile fish was observed by Hebert and Haffner (in press). They reported elevated levels in spottail shiners, brook silversides and bluntnose minnows collected at a location about 15 km below the Sarnia industrial complex compared to levels in fish collected at 2 locations in the Walpole Island marshes. As HCB and OCS inputs to the St. Clair River have been associated mainly with Dow Chemical (Environment Canada and Ministry of the Environment 1985), the elevated levels of these contaminants in the spottail shiners collected from locations below Suncor were likely due to Dow discharges of these chemicals. No spatial pattern was detected for HCE, all values being less than the detection limit.

FIGURE 4.4.17 HEXACHLOROBENZENE RESIDUE TRENDS IN YOUNG-OF-THE-YEAR SPOTTAIL SHINERS FOR THE ST. CLAIR RIVER AT LAMBTON GENERATING STATION. (MEAN  $\pm$  95% C.L.)

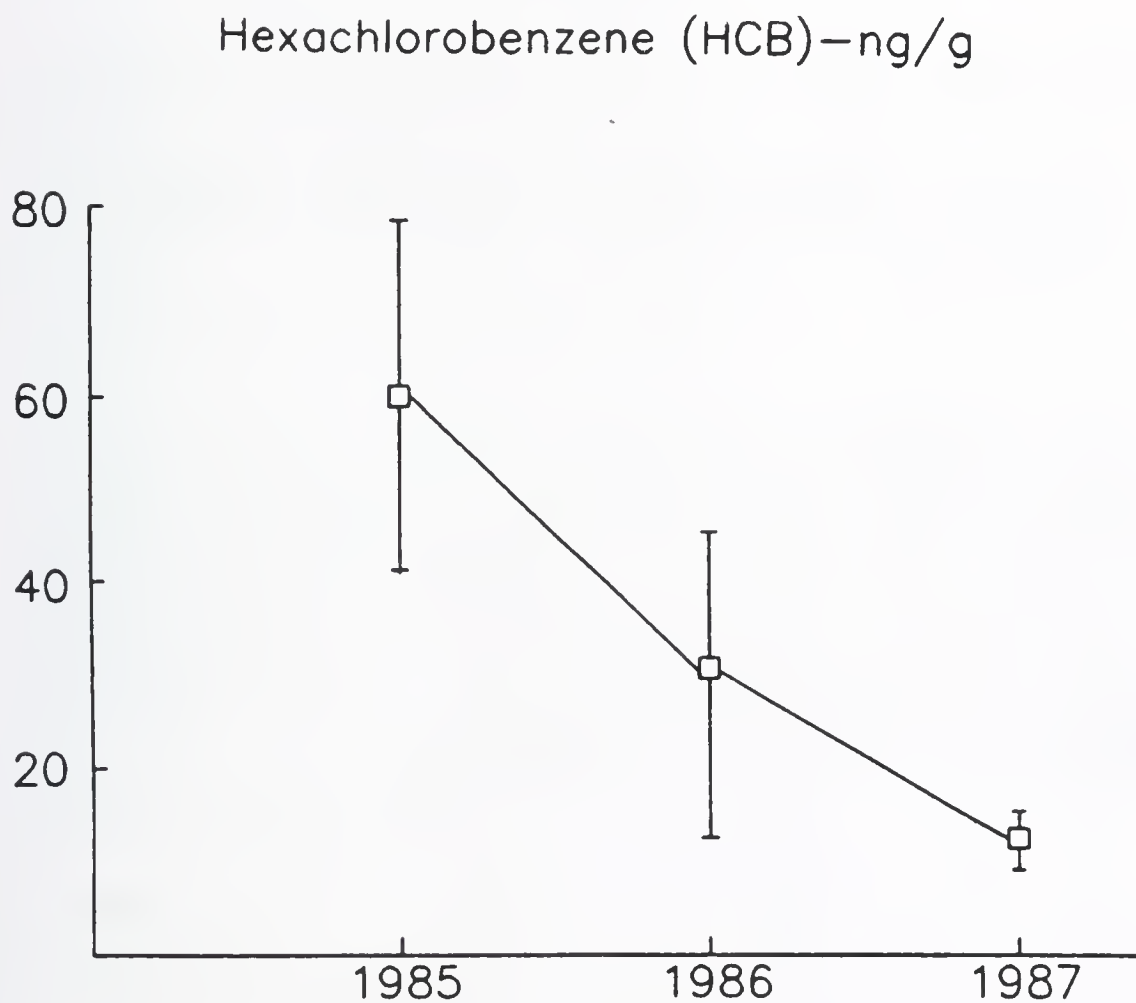
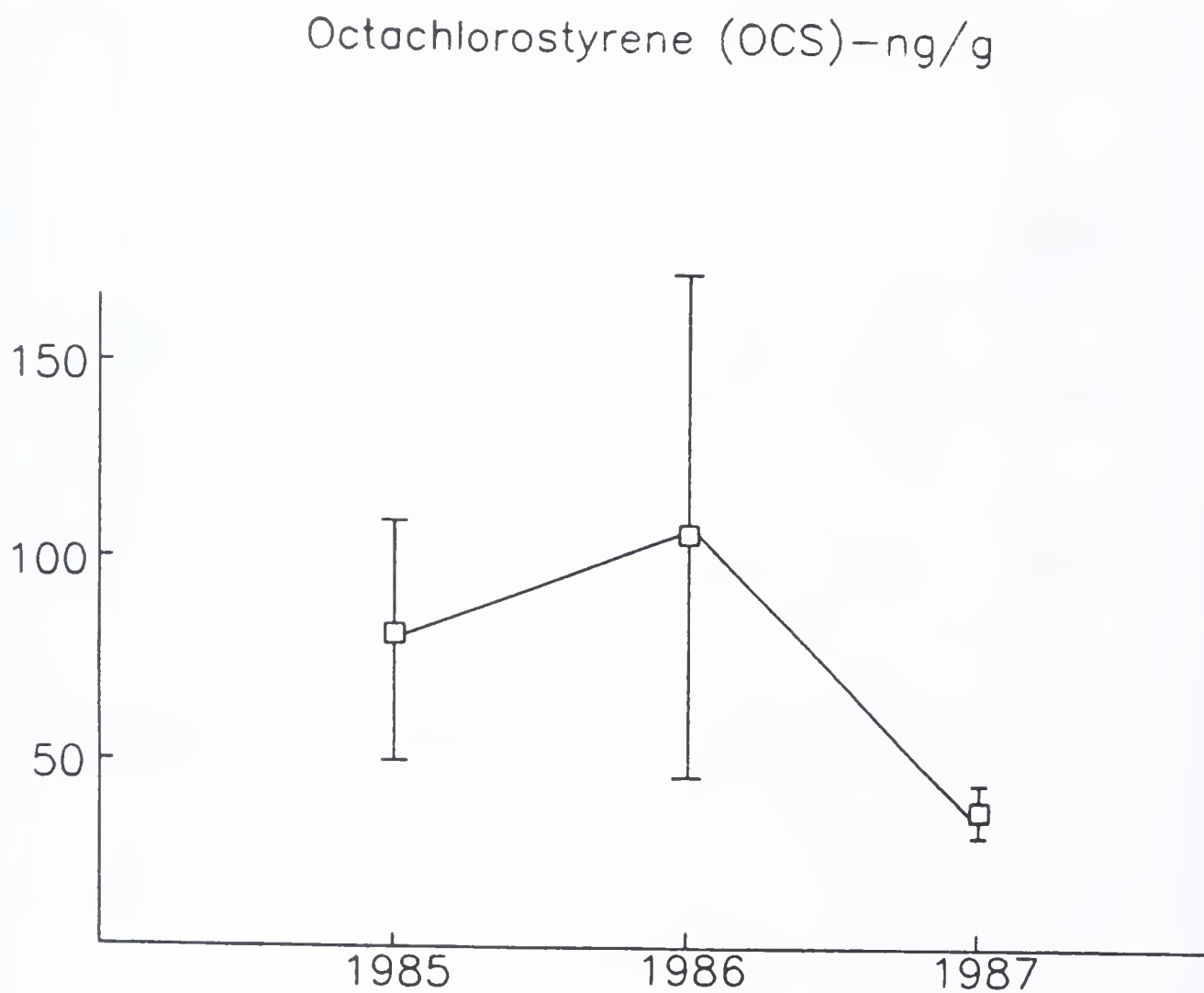


FIGURE 4.4.18 OCTACHLOROSTYRENE RESIDUE TRENDS IN YOUNG-OF-THE-YEAR SPOTTAIL SHINERS FOR THE ST. CLAIR RIVER AT THE LAMBTON POWER GENERATION STATION. (MEAN  $\pm$  95% C.L.)





Tetrachloroethylene residues in juvenile emerald shiners were found to be much elevated in the 1985 collection below the industrial complex (Table 4.4.17). These residue increases were associated with a major spill of TCE from Dow Chemical on August 13-16, 1985. Carbon tetrachloride residues in the 1986 shiner collections from the same sites were detected in only one of the samples, and there is no evidence from these data that inputs from the industrial complex exist.

Comparison of contaminant levels in juvenile spottail shiners with the New York State criteria for protection of piscivorous wildlife (Newell et al. 1987) showed that the HCB guideline of 330 ng/g was never exceeded. Levels of OCS in spottail shiners were above the 20 ng/g criteria at the Suncor, Lambton Generating and South Channel stations in all years. Exceedance of the 20 ng/g criteria implies a potential hazard for piscivorous wildlife.

While the data base is too small for proper trend assessment for most of the river collection sites, it may be noteworthy that HCB and OCS residue accumulations have declined at the Lambton Power generating Station. HCB residue concentrations in the 1987 spottail shiner collections were significantly ( $p < 0.01$ ) lower relative to the 1985 and 1986 residues. Similarly OCS residues in the 1987 collections were significantly ( $p < 0.01$ ) lower than OCS concentrations in the 1985 collections. No trends were evident for HCB and OCS in the Mitchell Bay collections. Too few data points were available for HCBD and HCE to assess temporal trends.

#### 4.4.10 Sportfish

##### (a) Introduction and Methods

Sportfish were collected under the MOE/MNR (Ontario Ministry of the Environment/Natural Resources) Sportfish Contaminants Program. This program is designed to inform the public about the safety of consuming fish from Ontario waters and since its inception in 1977 has tested

fish from over 1400 locations for a wide variety of contaminants. Fish were commonly collected by staff of the Ministry of Natural Resources using various netting procedures or sampled from a commercial fisherman's catch. Where possible, the collection included 15-20 fish with lengths and weights representative of the size range of the species from the location being tested. A boneless, skinless fillet of dorsal muscle flesh was removed, packaged and frozen for shipment to the MOE laboratories in Rexdale. Analyses were carried out according to the methods described in the "Outlines of Analytical Methods" (MOE 1981).

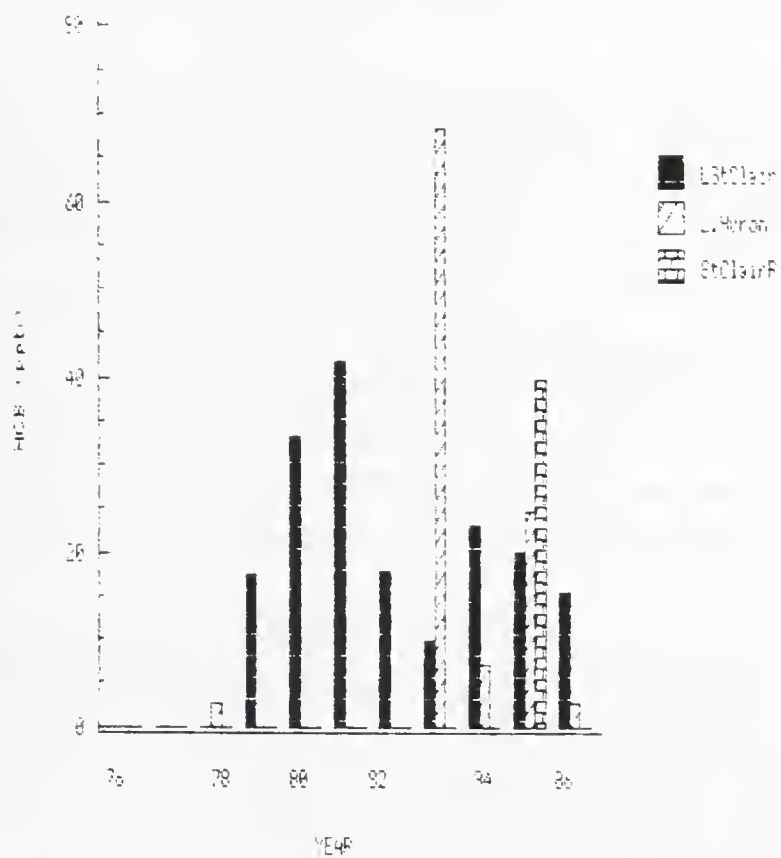
HCB and OCS are two key contaminants in the St. Clair River MISA Pilot Site study. Carp were collected for HCB analysis from southern Lake Huron in the Bright's Grove area in 1978, 1983, 1984, 1985 and 1986; from Lake St. Clair in 1979-1986 inclusive and from the St. Clair River near Stag Island in 1985 only. Channel catfish were collected for HCB analysis from southern Lake Huron in 1982-1985 inclusive, and from Lake St. Clair in 1976, 1977 and 1979-1986 inclusive.

Carp and channel catfish are good choices as biomonitors for this study because: i) they have the most complete length of record to establish temporal trends in contaminant burdens; ii) they likely reflect local environmental conditions as compared to some other sportfish which range more widely; iii) they generally have the highest levels of HCB and OCS among the various sportfish tested due to the higher fat content in their flesh.

#### (b) Results and Discussion

The average level of HCB in carp collected from the three locations is plotted by year in Figure 4.4.19. In 1985, when all three locations were sampled, concentrations of HCB in carp were highest at the Stag Island location, about twice as high as levels found in carp from the Lake Huron or Lake St. Clair locations. However, HCB levels in carp were not consistently higher at Lake St. Clair than in southern Lake Huron. In 1984 and 1986, HCB was higher in carp from Lake St. Clair whereas in 1983 and 1985 the opposite was true.

**Figure 4.4.19:** HCB in Carp from Lakes Huron, St. Clair and the St. Clair River.



At the Lake St. Clair location, no long-term trends for HCB in carp were evident. Several factors may be masking any spatial or temporal trends in the data. The method of expressing the data as the average concentration for a collection of fish may be biased if yearly biases occur in the size and age of individual fish that make up the collection. Furthermore, the uptake and depuration of HCB in carp on a short term basis may mask long-term trends.

The average values of HCB in channel catfish collected from Lake St. Clair were 5 - 10 fold higher than those in catfish from the southern portion of Lake Huron (Bright's Grove) (Figure 4.4.20). No clear trends in concentrations over time are evident. Data from the 1970's may be more a reflection of analytical recovery than quantitatively comparable to later data.

No criterion for HCB in fish to protect human consumers has been set by Health and Welfare Canada, although a criterion of 100 ppb exists for whole eggs. At no time or location did average levels of HCB in carp, catfish (or any other species) exceed the 100 ppb criterion for eggs. The U.S. EPA has established a draft value of 6.4 ppb for human consumption with an associated cancer risk of  $10^{-6}$ . This is somewhat more stringent than the  $10^{-5}$  health risk normally adopted by Health and Welfare Canada; however, it is based on average consumption levels of 6.5g/day. The average Ontario angler and certain native communities eat on average, 24.7 and 117g/day respectively.

Correcting the U.S. EPA  $1 \times 10^{-6}$  criterion of 6.4 ppb for HCB to a risk of  $1 \times 10^{-5}$  and adjusting for the higher rate of consumption by the average Ontario angler would result in a criterion of approximately 17 ppb. Some of the carp samples in all of the three locations tested (Figure 4.4.19) exceed this value. Lake St. Clair Channel Catfish from 1980 to 1986 annually averaged more than this approximate criterion. Adjusting for the high consumer level of 117 g/day would result in a criterion for HCB of 4 ppb. Maintaining a cancer risk of  $1 \times 10^{-6}$  would result in criteria of 1.7 and 0.4 ppb respectively.

Newell et al. (1987) developed fish flesh criteria for the protection of piscivorous wildlife based on feeding studies done with wildlife and laboratory animals. They set a non-carcinogenic fish flesh criteria of 330 ppb for HCB. Comparing this value to the data on HCB in sportfish from the St. Clair system, it is apparent that the average levels in sportfish never exceed the 330 ppb criterion.

The average level of OCS in carp collected from the three locations is plotted by year in Figure 4.4.21. In 1985 when all three locations were sampled, concentrations of OCS in carp were lower at the Stag Island location than concentrations in carp from either the Lake Huron or Lake St. Clair locations. No consistent spatial patterns were evident in OCS residues in carp. Levels were higher at the Lake Huron station in 1983 and 1984, higher at the Lake St. Clair station in 1986 and about the same at these two stations in 1985.

No temporal trend in OCS was evident in Lake St. Clair carp over the 1981-1986 period. However, a declining trend of OCS in the Lake Huron carp was evident over the 1983-1986 period. The concerns of variable size and age fish affecting the mean OCS value apply as they did for HCB.

The average value of OCS in channel catfish collected from Lake Huron and Lake St. Clair are plotted by year in Figure 4.4.22. OCS levels in channel catfish from Lake St. Clair were much higher than they were in channel catfish collected from southern Lake Huron at Bright's Grove. No temporal trends were evident at either location.

No criteria for OCS in fish to protect human consumers has been set by Health and Welfare Canada. Newell et al., (1987) developed a non-carcinogenic fish flesh criterion of 20 ppb OCS for the protection of piscivorous wildlife. The average value of OCS in carp exceeded this guideline in all years at all locations in the St. Clair system except in Lake Huron in 1986. The average value of OCS in channel catfish exceeded the guideline by 4-6 times in all years at the Lake St. Clair location. Channel catfish from Lake Huron did not exceed the 20 ppb guideline.

Figure 4.4.20: HCB in Channel Catfish from Lake Huron, and the St. Clair River.

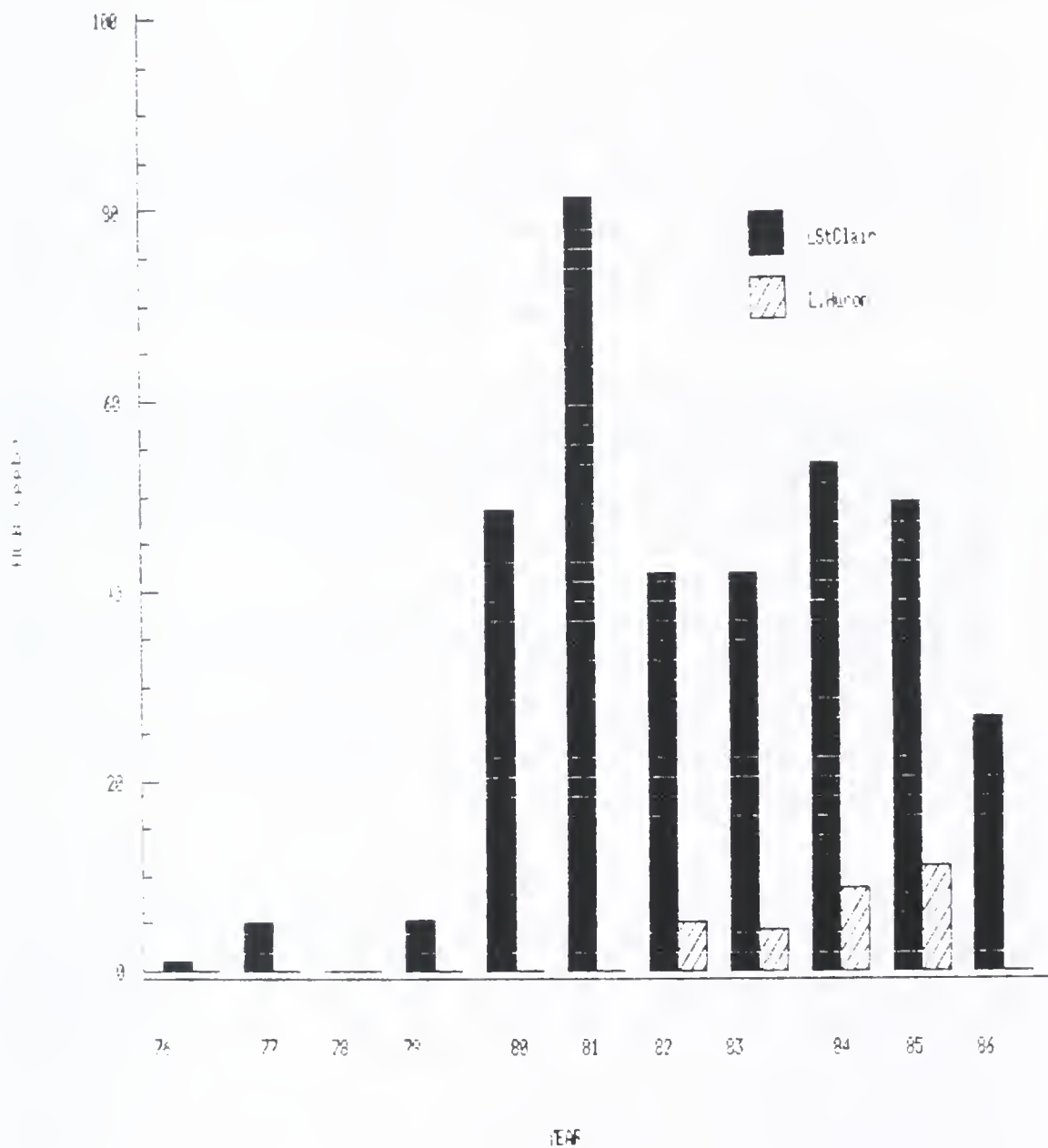


Figure 4.4.21: OCS in Carp from Lakes Huron, St. Clair and the St. Clair River.

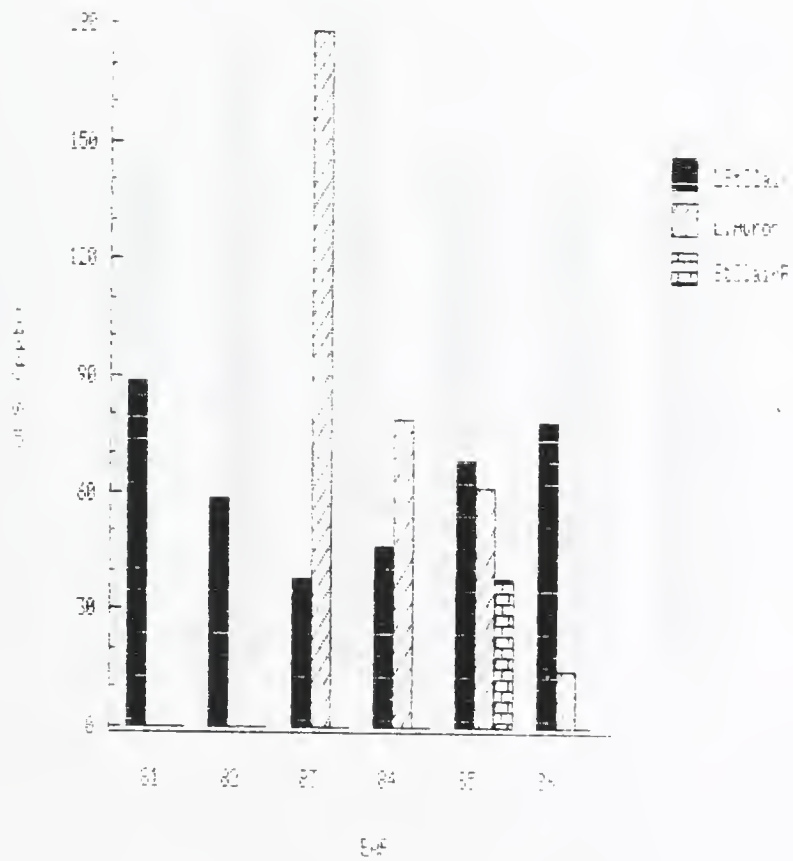
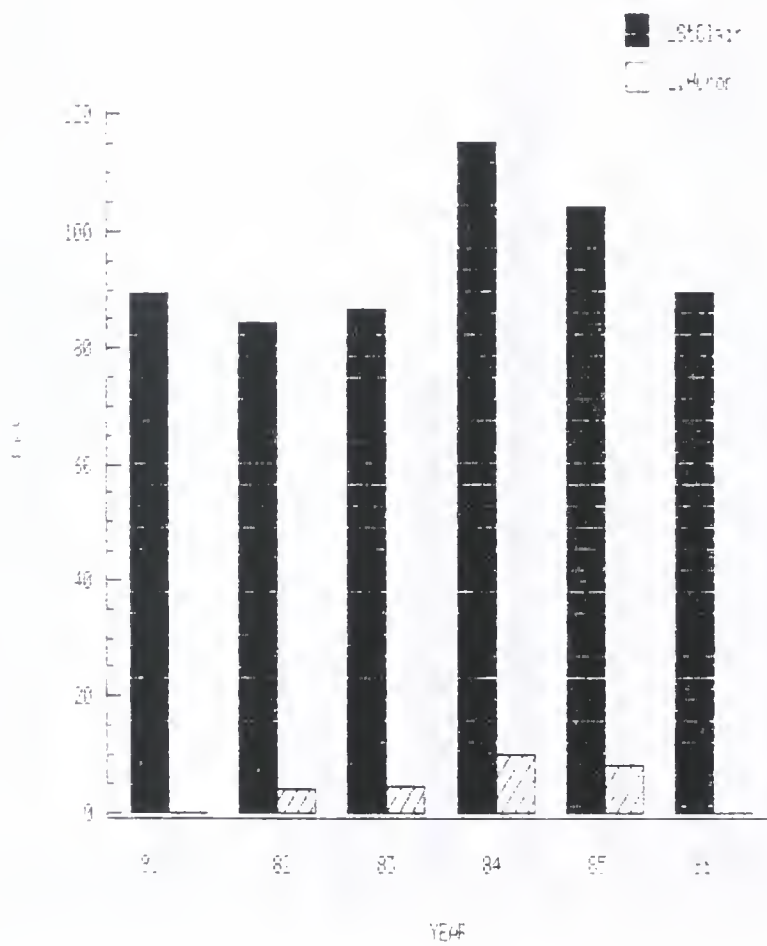




Figure 4.4.22: OCS in Channel Catfish from Lakes Huron, St. Clair and the St. Clair River.



It is clear that reliance on a single species, even if it is of high fat (lipid) content cannot always be relied upon to provide interpretable data. While the fluctuations of HCB and OCS in carp in Lake Huron (Bright's Grove) and Lake St. Clair rarely show any pattern, the data for channel catfish shows clearly that the Lake St. Clair specimens have, over a considerable number of years, been found to contain much more HCB and OCS than the same species from collections in southern Lake Huron.

#### 4.4.11 Mutagenicity Testing

##### (a) Introduction and Methods

Mutagenicity testing of Dow and Polysar effluents conducted in this MISA study was an extension of studies conducted on these effluents as a component of the St. Clair River Organic Study (MOE 1981b). In that study, the volatile organic fraction of effluent samples from Dow Chemical were concentrated a factor of 500 times using a purge and trap technique. Concentrates were tested for mutagenic activity using the Ames plate incorporation assay. The results of that study indicated that two of the current Dow chemical effluents, the 2nd and 4th street sewers possessed mutagenic activity.

In an attempt to detect mutagenic activity at ambient effluent concentrations the present mutagenicity testing study employed a modified, more sensitive version of the Ames test, the Fluctuation assay. This approach to the testing of effluents at ambient chemical levels was considered to be more suitable for the setting of effluent requirements through MISA.

Effluent samples from Dow and Polysar were collected in conjunction with the MISA sampling program over the period May through August 1986. Sampling dates are identified in Table 4.4.18. The samples were filter sterilized through 0.2 $\mu$  Teflon membrane filters and the sample pH was adjusted to 7.0 if necessary. Samples were tested for the presence of mutagenic activity using the Ames Fluctuation assay,

utilizing tester strains TA98 and TA100, both with and without metabolic activation, at sample doses of 2.5, 5.0, 10.0 and 15.0 mL. A negative control, spontaneous mutation, and a positive control, containing a known mutagenic compound, was included in each sample run. Fluctuation assay plates were incubated at 37°C for 7 days. Plates were scored for the number of positive wells, indicating the presence of mutated bacterial cells. Samples which demonstrated a significant increase ( $p < 0.01$  in the absence of S-9,  $p < 0.001$  in the presence of S-9) in positive wells with an increasing number of positive wells at increasing volumes of sample were scored mutagenic.

(b) Results and Discussion

The results of mutagenicity screening tests conducted on Dow and Polysar effluents are presented in Table 4.4.18. All samples were tested in the Fluctuation assay using strains TA98 and TA100, both with and without metabolic activation. When tested with strain TA100 in the absence of metabolic activation, both the Polysar Biox effluent and the Dow 4th Street effluent induced a significant increase in the number of positive wells, although a dose-related increase in the number of positive wells was not observed. All effluents were negative in strain TA98 without S-9 and all other effluents were considered non-mutagenic with TA100 in the absence of S-9.

With metabolic activation, zero control values for both strain TA98 and TA100 were considerably elevated compared to values for these strains in the absence of S-9. This elevation was probably the result of nutrients in S-9, likely histidine, which resulted in an apparent increase in the spontaneous mutation rate. To compensate for these elevated zero control values, only those responses significantly different from the zero control at  $p < 0.001$  were considered positive.

The Polysar Biox effluent induced a significant ( $p < 0.001$ ) increase in positive wells at more than one dose when tested with strain TA100 plus S-9. This response was considered to indicate mutagenic activity in this effluent. All other effluents were non-mutagenic with metabolic activation with both strains TA98 and TA100.

TABLE 4.4.18: MUTAGENICITY TESTING RESULTS, FLUCTUATION ASSAY, OF DOW CHEMICAL AND POLYSAR EFFLUENTS. RESULTS ARE EXPRESSED AS NUMBER OF POSITIVE WELLS PER PLATE IN A TOTAL OF 96 WELLS PER PLATE SIGNIFICANT DIFFERENCE FROM ZERO CONTROL PLATE:  
(a) =  $p < 0.05$ , (b) =  $p < 0.01$ , (c) =  $p < 0.001$ .

TESTER STRAIN TA98 - S-9

		POSITIVE WELLS PER PLATE					
SAMPLE	SAMPLE DATA	ZERO CONTROL	2NF 30 $\mu$ g	SAMPLE VOLUME			
				2.5ml	5.0ml	10.0ml	15.0ml
Polysar Intake	24/07/86	5	96	0	2	3	1
	27/08/86	4	95	2	2	3	2
Polysar Biox	29/05/86	7	96	1	4	1	10
	24/07/86	4	95	1	0	0	1
Polysar 66-inch Sewer Stereo API	18/08/86	4	95	5	1	3	1
	29/05/86	7	96	1	5	2	3
Polysar 72-inch Sewer	24/07/86	5	96	4	3	3	0
Township Ditch	29/05/86	7	96	3	3	2	1
Cole Drain	24/07/86	5	96	5	9	2	1
Dow 1st St. 42-inch Sewer 54-inch Sewer	10/06/86	6	96	2	3	0	2
	10/06/86	6	96	1	3	2	1
Dow 2nd St.	06/86	5	96	6	3	2	1
Dow 3rd St.	10/06/86	6	96	6	2	2	3
Dow 4th St.	06/86	5	96	4	2	2	5

TABLE 4.4.18: (cont'd)

TESTER STRAIN TA100 - S-9

		POSITIVE WELLS PER PLATE					
SAMPLE	SAMPLE DATE	ZERO CONTROL	NaN <sub>3</sub> 0.5µg	SAMPLE VOLUME			
				2.5mL	5.0mL	10.0mL	15.0mL
Polysar Intake	23/07/86	13	96	15	21	9	14
	27/08/86	7	94	15	11	13	12
Polysar Biox	29/05/86	15	95	18	20	7	1
	24/07/86	7	94	27 <sup>c</sup>	21	20	14
Polysar 66-inch Sewer Stereo API	18/08/86	7	94	13	19 <sup>b</sup>	7	6
	29/05/86	15	95	19	16	12	11
Polysar 72-inch Sewer	24/07/86	13	96	18	17	14	15
Township Ditch	29/05/86	15	95	9	15	18	14
Cole Drain	24/07/86	13	96	16	15	16	13
Dow 1st St. 42-inch Sewer	10/06/86	10	93	17	13	16	14
54-inch Sewer	10/06/86	10	93	20	11	13	15
Dow 2nd St.	06/86	6	94	12	11	7	12
Dow 3rd St.	10/06/86	10	93	19	12	15	9
Dow 4th St.	06/86	6	94	11	18 <sup>b</sup>	16 <sup>a</sup>	15 <sup>a</sup>

TABLE 4.4.18: (cont'd)

TESTER STRAIN TA98 + S-9

SAMPLE	SAMPLE DATE	POSITIVE WELLS PER PLATE					
		ZERO CONTROL	NaN <sub>3</sub>	SAMPLE VOLUME			
			0.5µg	2.5mL	5.0mL	10.0mL	15.0mL
Polysar Intake	24/07/86	31	96	26	23	18	22
	27/08/86	40	96	18	20	23	22
Polysar Biox	29/05/86	40	92	28	28	45	a 5
	24/07/86	31	96	31	42	31	38
Polysar 66-inch Sewer Stereo API	18/08/86	40	96	36	38	34	20
	29/05/86	40	92	28	27	21	22
Polysar 72-inch Sewer	24/07/86	31	96	37	22	27	20
Township Ditch	29/05/86	40	92	26	28	20	29
Cole Drain	24/07/86	31	96	32	21	20	22
Dow 1st St. 42-inch Sewer	10/06/86	40	92	34	30	25	24
54-inch Sewer	10/06/86	40	92	35	29	25	22
Dow 2nd St.	06/86	30	77	29	30	20	16
Dow 3rd St.	10/06/86	40	92	30	30	27	21
Dow 4th St.	06/86	30	77	26	29	16	25

TABLE 4.4.18: (cont'd)

TESTER STRAIN TA100 + S-9

SAMPLE	SAMPLE DATE	POSITIVE WELLS PER PLATE					
		ZERO CONTROL	NaN <sub>3</sub> 0.5µg	SAMPLE VOLUME			
				2.5mL	5.0mL	10.0mL	15.0mL
Polysar Intake	24/07/86	43	96	<sup>a</sup> 57	48	52	<sup>a</sup> 57
	27/08/86	58	96	43	41	53	53
Polysar Biox	29/05/86	42	89	55	<sup>c</sup> 64	54	<sup>c</sup> 75
	24/07/86	43	96	<sup>c</sup> 68	<sup>c</sup> 65	<sup>c</sup> 86	<sup>c</sup> 84
Polysar 66-inch Sewer	18/08/86	58	96	50	<sup>b</sup> 59	55	52
Stereo API	29/05/86	42	89	53	<sup>a</sup> 55	52	<sup>b</sup> 59
Polysar 72-inch Sewer	24/07/86	43	96	48	47	<sup>b</sup> 61	<sup>a</sup> 57
Township Ditch	29/05/86	42	89	50	54	53	49
Cole Drain	24/07/86	43	96	48	51	<sup>b</sup> 62	<sup>a</sup> 59
Dow 1st St. 42-inch Sewer	10/06/86	42	89	54	50	<sup>a</sup> 57	<sup>a</sup> 55
54-inch Sewer	10/06/86	42	89	<sup>a</sup> 55	54	<sup>a</sup> 55	<sup>b</sup> 59
Dow 2nd St.	06/86	50	92	52	42	40	45
Dow 3rd St.	10/06/86	42	89	50	43	40	53
Dow 4th St.	06/86	50	92	42	37	49	35



Based on the fluctuation test results, two effluents, the Polysar Biox effluent and the Dow 4th Street effluent, were considered to contain mutagenic activity at ambient effluent concentrations. The Polysar Biox effluent was considered mutagenic in strain TA100, both with and without metabolic activation. The Dow 4th Street effluent was considered mutagenic with strain TA100 without metabolic activation. All other effluents were considered non-mutagenic under the test conditions.

The results of this current mutagenicity testing study were compared to those of the 1981 St. Clair River Organic Study. In both studies, the Dow 4th Street effluent was shown to contain mutagenic activity. The Dow 2nd Street effluent, found to contain mutagenic activity in the 1981 study, was not mutagenic in the current study. The Polysar Biox effluent, not operational during the 1981 study was found to contain mutagenic activity in this current study. Unlike the 1981 study, which required a 500 fold concentration of volatile organics to detect mutagenic activity in these effluents, this current study employing the Fluctuation mutagenicity assay, has detected mutagenic activity in two effluents at ambient effluent concentrations.



## 5.0 DISCUSSION OF RESULTS FOR SPECIFIC CHEMICALS OF CONCERN

### 5.1 Rationale for Selection of Compounds

As part of the MISA Program, the Ministry of the Environment identified a list of contaminants of greatest concern based on combined exposure and effects concerns for Ontario. This list, and the rationale for its development are contained in the report entitled "Effluent Monitoring Priority Pollutant's List" (EMPPL 1987).

The EMPPL includes a total of 37 compounds identified in a preliminary report of findings from the St. Clair River pilot site (MOE 1987). An abbreviated list of four contaminants of potential concern from pilot site findings was selected for detailed review: hexachlorobenzene (HCB); hexachlorobutadiene (HCBd); octachlorostyrene (OCS) and tetrachloroethylene (PERC).

Each of these compounds has been identified in industrial effluents discharged from Dow Chemical to the St. Clair River as part of this investigation (Sections 4.1.1 and 4.1.2) as well as by numerous other investigators (Bonner and Meresz 1980; Munro et al. 1985; King and Sherbin 1986; DOE/MOE 1986; King and Edwardson 1988).

These materials arise from anthropogenic sources and occur as intermediate or end products primarily in the manufacture of chlorinated solvents (Table 5.1.1).

In order to adequately document the level of concern associated with each of these materials, a brief summary of physical/chemical and toxicological information was assembled (Tables 5.1.2 - 5.1.3). These "effects" data, along with the exposure data referred to above, provided a desktop hazard assessment and supported the selection of this priority list of chemicals.

TABLE 5.1.1: PRODUCTION AND USE OF CHEMICALS OF POTENTIAL CONCERN

PRODUCTION/USES

- 
- |      |   |
|------|---|
| HCB  | <ul style="list-style-type: none"> <li>• A primary constituent of the tarry residue formed in the production of chlorine for chlorinated solvents, such as tetrachloroethylene.</li> <li>• Used as a seed protectant; fungicide; intermediate in dye and synthetic rubber manufacture; plasticizer for PVC.</li> </ul>            |
| HCBD | <ul style="list-style-type: none"> <li>• Intermediate product in the manufacture of chlorine for chlorinated solvents, such as tetrachloroethylene. Not known to occur naturally.</li> <li>• Used as a solvent for elastomers; heat transfer fluid; transformer and hydraulic fluid; wash liquor for hydrocarbons</li> </ul>      |
| OCS  | <ul style="list-style-type: none"> <li>• Constituent of tarry residue formed in the production of chlorine for chlorinated solvents such as tetrachloroethylene.</li> </ul>   |
| PERC | <ul style="list-style-type: none"> <li>• Principle intermediate product resulting from the chlorinolysis reaction of a hydrocarbon feedstock with excess chlorine under extreme conditions.</li> <li>• Tetrachloroethylene is used in the dry cleaning industry; as well as for metal degreasing and textile cleaning.</li> </ul> |
-

TABLE 5.1.2: SELECTED PARAMETERS OF POTENTIAL CONCERN:  
PHYSICAL/CHEMICAL CHARACTERISTICS

CHEMICAL PROPERTY	C H E M I C A L			
	HCB <sup>1</sup>	HCBD <sup>2</sup>	OCS <sup>2</sup>	PERC <sup>5</sup>
Molecular Wt.	284.76	260.76	379.68	165.83
Solubility @ 25C°	0.006 ppm	2 ppm <sup>3</sup>	2.5 ppb;- 7.5 ppb	150 ppm
Vapour Pressure @ 25C° (mmHg)	2.1X10 <sup>-5</sup>	0.15(@20C°)	N/A	14 (@20°C)
Log K <sub>ow</sub>	5.2-6.4	4.90	6.29	2.6 <sup>4</sup>
Density @ 20-25C°	2.044	1.55	N/A	1.62
Melting pt. C°	230	-21	99-101 <sup>6</sup>	-22.7
Boiling pt. C°	322	215	N/A	121.4
T <sub>½</sub> water fish tissue	60-70 days <sup>2</sup>	3-300 days	90-120 days	27±3 mins <sup>4</sup> <24 hours <sup>3</sup>

<sup>1</sup> CESARS 1989

<sup>2</sup> HSDB 1987

<sup>3</sup> CCREM 1987

<sup>4</sup> Wells, D.L. 1985

<sup>5</sup> Verschueren 1977

<sup>6</sup> Sitwell 1982

<sup>7</sup> Niimi and Palazzo 1985

N/A - Not Available

TABLE 5.1.3: SELECTED PARAMETERS OF POTENTIAL CONCERN:  
SUMMARY OF AQUATIC TOXICOLOGICAL INFORMATION

	HCBI <sup>1</sup>	HCBD <sup>2</sup>	OCS <sup>2</sup>	PERC <sup>3</sup>
ACUTE TOXICITY (ppm)				
• 96hr LC <sub>50</sub>				
<u>Daphnia magna</u>	-	-	-	18.1(48 hr)
Fathead minnows	22*	0.09	0.7-0.74 <sup>8</sup>	13.5
Channel catfish	14*	-	-	-
Bluegill	12*	-	-	-
Rainbow trout	2.3*	0.32 <sup>3</sup>	-	4.99
Coho salmon	>50*	-	-	-
<u>Nitrocras spinipes</u>	-	-	0.034-0.15 <sup>7</sup>	-
CHRONIC EFFECTS (ppm)				
• LOAEL- <u>Daphnia magna</u>	0.016			
• NOEL - <u>Daphnia magna</u>				0.5-1.1
• MATC -		0.009 <sup>6</sup> (pond snail)		0.840 <sup>6</sup> (Bluegill)
• NOAEL- Rat			0.5	
• Carcinogenicity				
Mice and Hamsters	+ve			
Human		suspected		
Rat		+ve		
• Mutagenicity	+ve,-ve	+ve Ames	-ve Ames	+ve bacteria
• Teratogenicity	-			
• Bioconcentration				
Fathead minnows	5500-45700	6988.6 <sup>3</sup>	33113 <sup>4</sup>	61.5
Rainbow trout	7880	5800-17000		
• Enzyme Induction	+ve <sup>5</sup>		+ve	

1) CESARS 1989

2) HSDB 1987

3) EPA 1984

4) Pers. Comm., F.A.P.C. Gobas

\* Above water saturation for solubility

5) Courtney 1979

6) EPA 1980

7) Tarkpea et al. 1985

8) QSAR 1989

- Not available

## 5.2 Documentation of Sources

Hexachlorobenzene, HCB and OCS are intermediate or end products in the manufacture of tetrachloroethylene (perc) from Dow Chemical at Sarnia, Ontario. This facility is the only documented producer of tetrachloroethylene in the province and one of two in Canada. The other producer of chlorinated solvents is situated in Shawinigan, Quebec.

The occurrence and range of effluent concentrations from sources in the St. Clair River have been well documented. A comparison of current (1986-87) with earlier (1985) loadings indicates significant reductions for HCB (91%); HCB (81%); OCS (16%) and PERC (78.5%) from the Dow complex (see Section 4.1.1). This is due largely to improved environmental control, including separation of process and wastewater streams, enhanced waste treatment and spill containment facilities. Significant incidental reductions have been realized as part of a spill containment system which involves holding process wastewater in a surface pond for several days prior to discharge to the St. Clair River. This provides a spill buffer while also promoting volatilization of compounds to the atmosphere and/or settling on particulates. Tetrachloroethylene is the least hydrophobic (150 ppm solubility - Table 5.2.2) and most volatile compound while the other three compounds are very insoluble and likely to adsorb to suspended material.

Since 1984, loadings of HCB have been reduced even more substantially when one considers empirically estimated loadings during 1984 were on the order of 0.8 to 2.0 kg/day from the Dow 1st St. complex.

### 5.2.1 Spills

While it is recognized that daily or monthly average loadings reflect the range of typical operating conditions, episodic upsets or spills may contribute large quantities of material to the receiver.



In order to evaluate their significance, an inventory of spills of hazardous material in excess of 10 tons was assembled as part of the St. Clair River Pollution Investigation Report (DOE/MOE 1986). In the period from 1974 to 1985 in excess of 11,600 tons of potentially hazardous materials were spilled with 65% not recovered.

During 1986, 48 surface water spills from Ontario and Michigan sources were reported to have reached the St. Clair River including raw sewage, non-PCB containing oils and various chemical compounds. Industrial spill volumes ranged from 2 to 25,000 litres with minimal recovery while municipal bypasses discharged up to 433,000 l/hour at the Marine City, Michigan Waste Water Treatment Plant (UGLCCS 1989).

It is readily apparent that a single spill of any magnitude which goes unrecovered could approach or exceed the annual load of a particular compound.

As an example, the Dow spill of tetrachloroethylene in August 1985 resulted in approximately 2,270 l (3,670 kg) of unrecovered material. Average point source loadings in November 1985 amounted to approximately 14.2 kg/day from the Dow complex. This single episode amounted to the equivalent of 259 days of average point source inputs, and would have been substantially more in the event that less of the material had been recovered.

A series of workshops hosted by the International Joint Commission from 1986 to 1989 have addressed "Human-Machine" aspects as they relate to spills. Proceedings from the first two workshops (IJC 1988) have drawn similar conclusions based on the findings of King and Sherbin (1986) when compared to losses which occur as a result of spills. In one instance, a spill of styrene from Polysar released a load equivalent to 1328 years of continuous discharge.

### 5.2.2 Contaminated Sediments

Sediments in the vicinity of outfalls at Dow Chemical have been subject to elevated loadings of a number of contaminants for many years.

Some materials such as mercury have been observed at lower concentrations in surface core sections while higher levels are measured in deeper and older sediments (DOE/MOE 1986). The reverse appears to be true for contaminants such as HCB and OCS which are highest in most recent sediments (Oliver and Pugsley 1986).

These contaminated surficial sediments are subject to resuspension and may therefore introduce additional loadings to the water column. The contribution, while relatively minor in this instance due to high water column concentrations, becomes more important as additional point source control is attained. A quantitative assessment of this sediment-water interaction is provided in the discussion of load allocations (Section 6.2.1). Knowledge of the partitioning of specific contaminants, rates of resuspension and hydrodynamic characteristics enables this effect to be simulated through modelling.

In an effort to better understand this interaction, Dow Chemical, at the request of the Ministry of the Environment undertook a review of current literature to evaluate the significance of these contaminated sediments. The review has indicated that the contribution to the water column from Point Sources is much more significant than the contribution from the sediments.

### 5.2.3 Non-Point Sources

Concern over the importance of non-point source pollution prompted the inclusion of Annex 13 to the Great Lakes Water Quality Agreement (Revised November 1987).

In response to concerns over potential contamination from landfills and deep well disposal zones in the Chemical Valley, a number of investigations have been conducted.

Phase I draft reports addressing contaminant sources to the Township and Scott Road ditches which enter the Cole drain, as well as potential for contamination of the freshwater aquifer have been submitted for review and are discussed in the UGLCCS final report.

The occurrence and degree of contamination entering the St. Clair River from Ontario tributaries was investigated in a 1984-1985 study by the MOE. Results which were included in the UGLCCS report confirm findings of this study identifying the Cole drain as a major source of higher chlorinated hydrocarbons such as HCB, HCB<sub>D</sub>, HCE and OCS. While sources entering the Cole drain are being or have been documented, and measures taken to implement their control, the occurrence of HCB, OCS and PCBs in whole water and suspended solids from Talfourd Creek is of concern. Instantaneous loadings of HCB measured during 1984-85 at the mouth of Talfourd Creek were similar in magnitude to all Dow sewers except the 42-inch and 4th St. outfalls (Johnson and Kauss 1989).

### 5.3 Occurrence in the Environment - Discussion on a Chemical Specific Basis

Hazard assessment considers factors such as persistence and the propensity to accumulate in biological tissues. While persistence itself is not sufficient to deem a chemical "hazardous" (EMPPL 1987), it is an important consideration. Bioaccumulation and subsequent food-chain accumulation may yield biological tissue residues in higher trophic levels which are hazardous to the health of individuals and/or populations.

Figures 5.3.1 and 5.3.2 provide a comparison of specific chemical concentrations (max, mean, min) in various media. These media include, suspended solids in both effluents and receiving water; sediments; total seston; Cladophora; rooted macrophytes; clams and juvenile fish. For

purposes of comparison, only samples which were obtained in the reach between the Cole drain and the southern Suncor property line were considered. As indicated in the figure legends, results were not corrected on a dry weight basis.

#### 5.3.1 Hexachlorobenzene

The highest HCB concentrations were measured in surficial sediments 200m downstream of the Dow 1st St. complex. A measured value of 228 ppm at this location raised the overall mean above that of suspended solids both in the river and in sewer discharge (Figure 5.3.2).

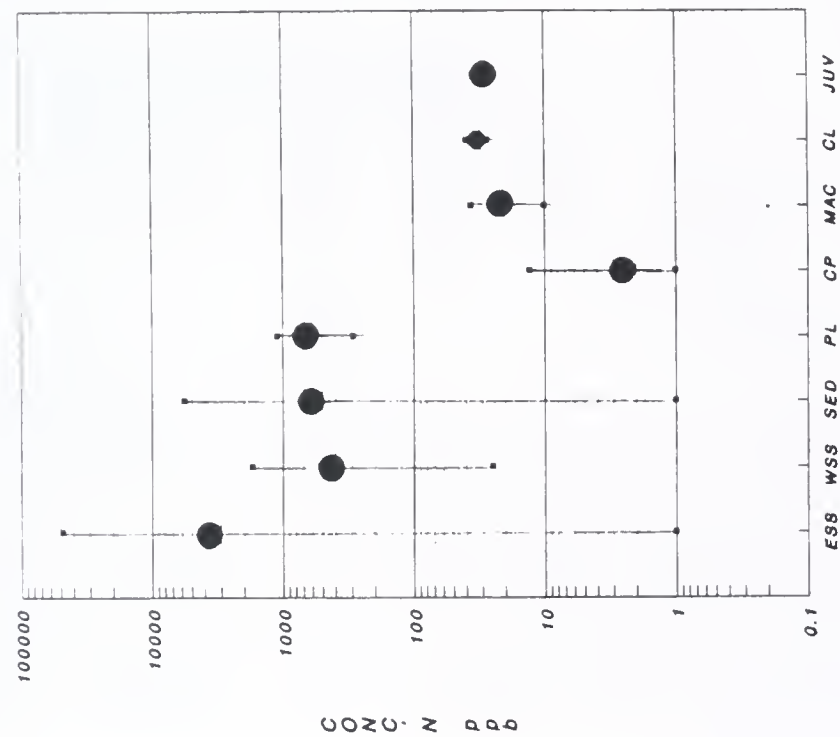
HCB is very hydrophobic, with a log  $K_{ow}$  of 5.2–6.4 as measured by a number of investigators (CESARS 1988). This results in partitioning to non-aqueous fractions such as suspended material and biological tissue.

Results of centrifugation in both effluent (Section 4.1.2) and receiving water (Section 4.2.1), generally attribute 100% of the HCB load to suspended material. This may be a function of the state of equilibrium of the contaminant load; however, it appears that process water from Dow passing through the Block 90 pond will have had sufficient retention time (approximately 2 days) to adsorb to particulate matter, prior to discharge to the St. Clair River.

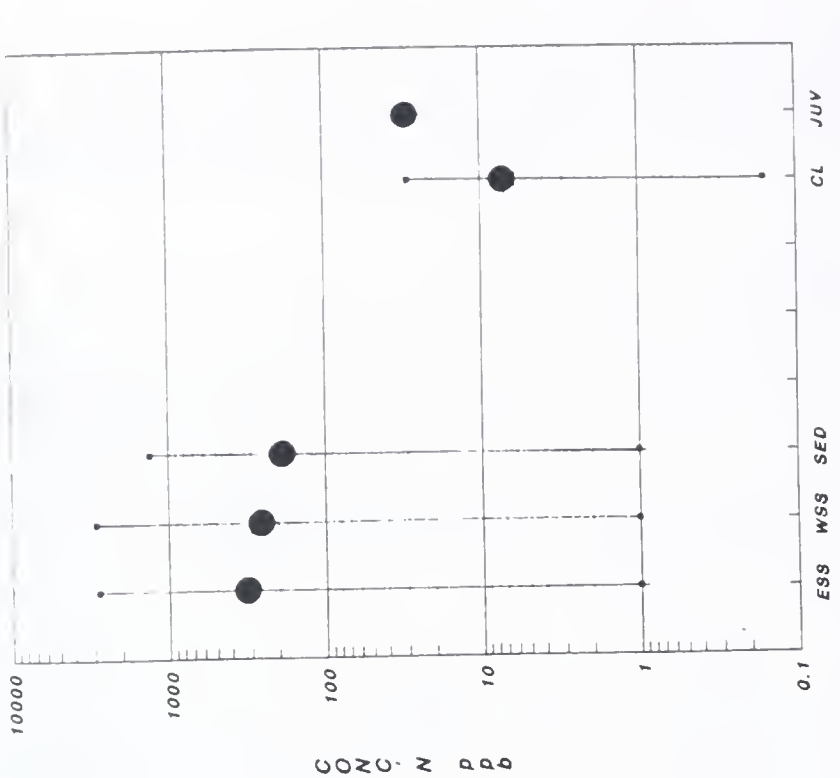
##### (i) Comparison with Guidelines

Sediment concentrations exceeded a draft HCB guideline of 0.02 ppm under consideration by the MOE, for the protection of benthic invertebrates, in 87% of samples obtained from the Polysar to Dow reach (n=38). At a control station (202) and at two stations downstream of the Lambton Generating Station, the criteria was not exceeded.

FIGURE 5.3.1: COMPARISON OF PARAMETERS OF CONCERN  
IN THE ST. CLAIR RIVER FROM POLYSAR TO SUNCOR  
BY MEDIA (MAX, MEAN, MIN)  
Dry weight



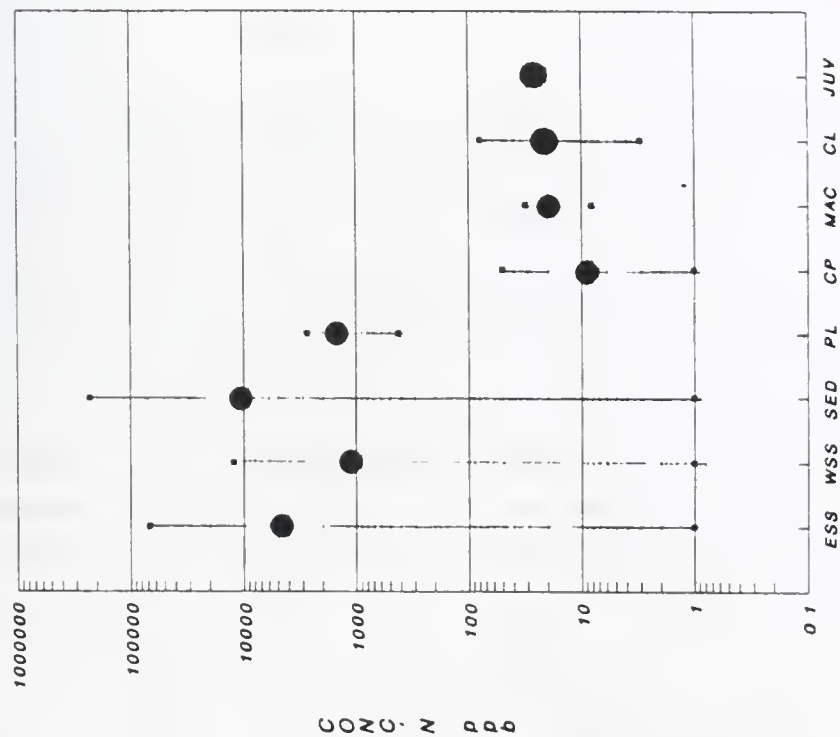
### OCTACHLOROSTYRENE



### TETRACHLOROETHYLENE

- LEGEND
- ESS - SUSPENDED SOLIDS (EFFLUENT)
  - WSS - SUSPENDED SOLIDS (WATER)
  - SED - SEDIMENTS
  - PL - PHYTOPLANKTON (SESTON)
  - CP - CLADOPHYTES
  - MAC - MACROPHYTES
  - CL - CLAMS
  - JUV - JUVENILE FISH
  - - values expressed on a wet weight basis

FIGURE 5.3.2: COMPARISON OF PARAMETERS OF CONCERN  
IN THE ST. CLAIR RIVER FROM POLYSAR TO SUNCOR  
BY MEDIA (MAX, MEAN, MIN)  
Dry weight



### HEXACHLOROBENZENE

#### LEGEND

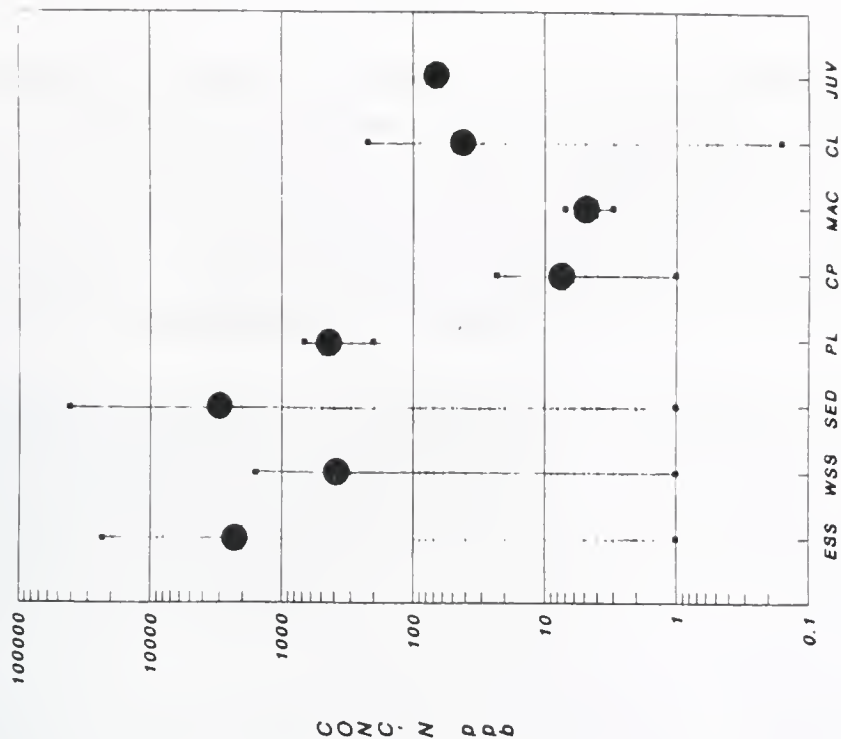
ESS - SUSPENDED SOLIDS (EFFLUENT)

WSS - SUSPENDED SOLIDS (WATER)

SED - SEDIMENTS

PL - PHYTOPLANKTON (SESTON)

CP - values expressed on a wet weight basis



### HEXACHLOROBUTADIENE

CP - CLAMMORIS

MAC - MACROPHYTES

CL - CLAMS

JUV - JUVENILE FISH

CP - values expressed on a wet weight basis



Two guidelines were considered in assessing the impact of HCB on biota. The U.S. EPA has recommended a fish consumption guideline for the protection of human health ( $10^{-6}$  cancer risk) of 6.4 ppb in the edible portion of fish tissue. A less restrictive guideline of 330 ppb has been established by the New York State Department of Environmental Conservation (NYS DEC) for the protection of piscivorous wildlife.

In evaluating the impact on biota, Cladophora, macrophytes, clams and juvenile fish results were pooled for comparison to New York State guidelines. Sportfish were collected from the St. Clair River during 1985 and would not reflect current (1986-1987) loadings. The more restrictive HCB guideline (6.4 ppb) was exceeded in the St. Clair River during 1985 and Lake St. Clair during 1985 and 1986 for both Carp (Cyprinus carpio) and Channel Catfish (Ictalurus punctatus). Lower tissue concentrations were observed in fish collected from lower Lake Huron. This guideline was exceeded for both species during 1985 (not collected during 1986). This likely reflects the somewhat transitory nature of these larger fish. No biological samples exceeded the NYS DEC guideline of 330 ppb for the protection of piscivorous wildlife.

When assessing the information derived from these guideline comparisons, it is likely more informative to compare biological and sediment results since they represent relatively recent, time-integrated data. Grab water samples may under- or overestimate the severity of conditions since they represent only an instant in time.

The Provincial Water Quality Objective (PWQO) of 6.5 ng/L for the protection of aquatic life was exceeded in 35 of 198 water samples (17.6%) between Polysar and Suncor obtained during the Investigative component. The furthest point downstream at which an exceedence was noted occurred at Station 216, approximately 1,200 m downstream of the Dow 1st St. complex. This sample was obtained within 20 cm of the river bottom while a coincident surface sample contained no detectable HCB. This depth relationship is outlined in Section 4.2.2 and appears



most pronounced for HCB. A high specific gravity for HCB (2.044) coupled with its hydrophobic nature likely resulted in a pronounced settling effect with much of the contaminant load carried on fine particulates. A similar relationship was observed for HCB, appearing more pronounced in May and October when the greatest temperature differential between effluent and receiving water occurs.

While temperatures were not recorded during the 1986 investigation, a follow-up study in May 1988 indicated a  $\Delta t$  of 7.7 C° likely resulting in a buoyant plume. Temperatures encountered in the July 1986 cruise would have resulted in a neutral plume and a less distinct vertical zonation, due to increased river temperatures.

It is difficult to discern the important factors in the behaviour of contaminants; however, the sensitivity analysis of load allocations provided in Section 6.2.1, discusses some of these variables. Figure 5.3.3 provides the range of observed concentrations in various media sampled throughout the study. The highest biological levels occurred in phytoplankton (total seston) >20  $\mu$ m in diameter with a peak concentration of 2,700 ng/g and a mean concentration of 1700 ng/g (Figure 5.3.2). This value also reflects other material in suspension greater than 20  $\mu$ m including organic and inorganic detritus. These two fractions are more accurately total seston since no microscopic sorting was undertaken to isolate plankton.

A progressive increase in mean biological tissue residue levels occurs in the following sequence (note: this figure is not intended to represent a food chain, it simply presents information based on findings from this study):

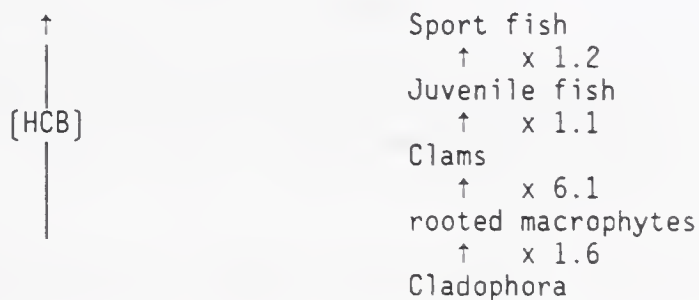


TABLE 5.3.1 - FREQUENCY OF EXCEEDANCE OF MEDIA-SPECIFIC CRITERIA  
FROM SAMPLES OBTAINED: A) BETWEEN POLYSAR AND SUNCOR;  
B) IN THE REMAINDER OF THE RIVER (1986)

<u>Hexachlorobenzene</u>			
Criteria	<u>WATER %</u> 0.0065 <sup>1</sup> ppb	<u>SEDIMENT %</u> 0.02 <sup>2</sup> ppm	<u>BIOTA* %</u> 0.33 <sup>3</sup> ppm
A) Polysar to Suncor	17.6% (199)	87% (38)	0% (45)
B) Remainder	0% ( 81)	0% ( 7)	0% (58)
<u>Hexachlorobutadiene</u>			
Criteria	<u>WATER %</u> 0.1 <sup>4</sup> ppb	<u>SEDIMENT %</u> NA	<u>BIOTA* %</u> 1.3 <sup>3</sup> ppm
A) Polysar to Suncor	1% (195)		0% (35)
B) Remainder	0% ( 79)		0% (79)
<u>Octachlorostyrene</u>			
Criteria	<u>WATER %</u> 0.1 <sup>6</sup> ppt	<u>SEDIMENT %</u> NA	<u>BIOTA* %</u> 0.02 <sup>3</sup> ppm
A) Polysar to Suncor			69% (13)
B) Remainder			40.3% (62)
<u>Tetrachloroethylene</u>			
Criteria	<u>WATER %</u> 260 <sup>4</sup> 8 <sup>5</sup> ppb ppb	<u>SEDIMENT %</u> NA	<u>BIOTA* %</u> NA

A) Polysar to Suncor 0% (212) 7%  
B) Remainder 0% ( 72) 0%

\* "Biota" includes Clams; macrophytes; Cladophora; Hexagenia, sculpins and juvenile fish.

- 1) MOE Provincial Water Quality Objective for the protection of aquatic life.
- 2) Draft value under consideration by MOE for the protection of benthic organisms.
- 3) New York State fish flesh criteria for the protection of piscivorous wildlife.
- 4) CCREM water quality guideline for the protection of aquatic life.
- 5) E.P.A. human health guideline (10<sup>-5</sup> cancer risk).
- 6) MOE advisory requires additional toxicological detail for guideline/objective development.

NA: Not Available

Note: "Remainder" includes locations upstream of Polysar and downstream of Suncor.

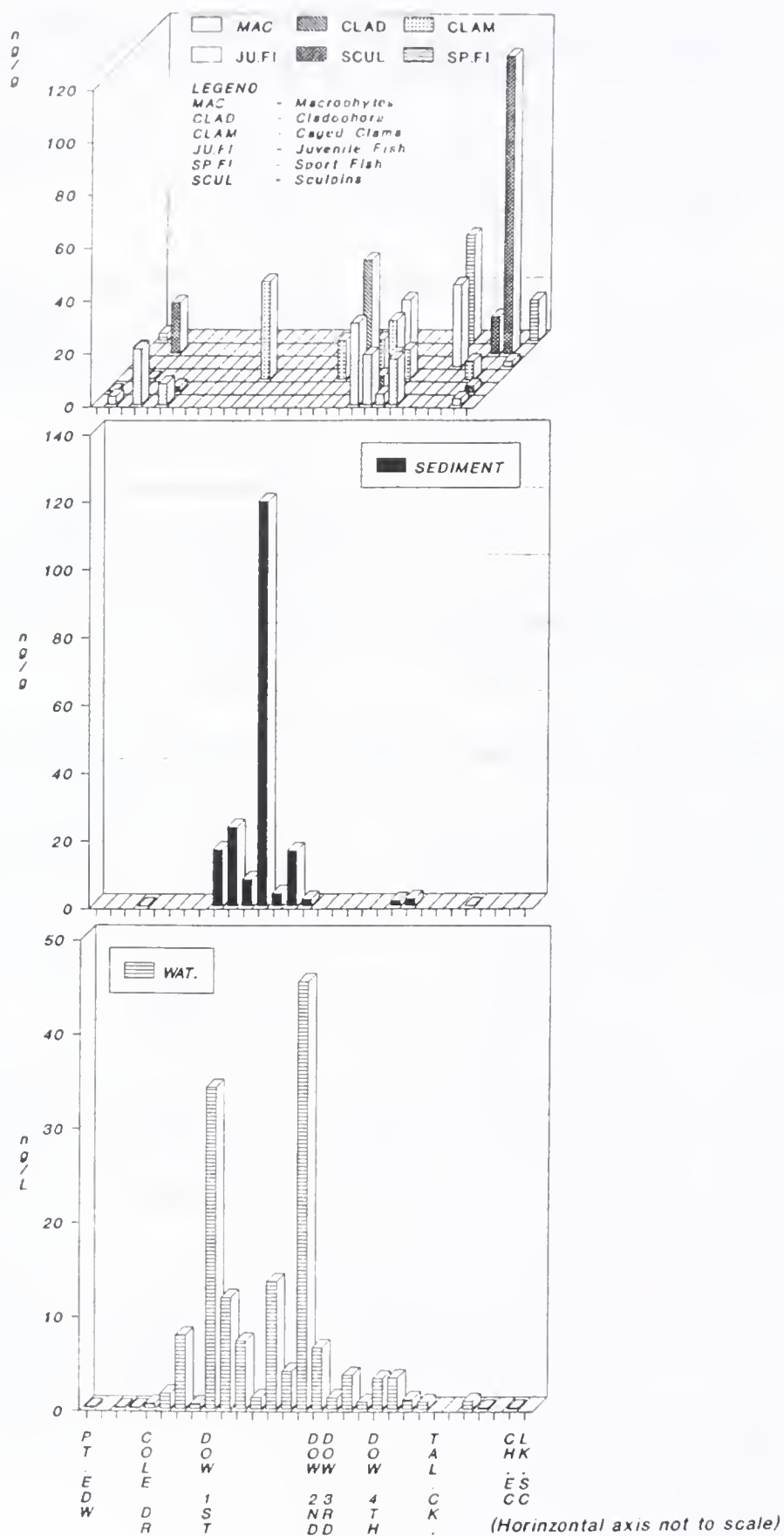
While these differences may not be statistically significant, the trend is consistent with what might be expected to occur for a highly bioaccumulative contaminant in the food chain. A more significant increase between levels would occur if clams, juvenile and sportfish were adjusted to dry weight values.

The integration of contaminants with time is evident, as the range of measured values in biota is much narrower than in the bottom sediments and suspended solids. These latter ranges reflect the highly variable sources in the vicinity.

Violations of existing criteria for sediment and biota, and to a lesser extent, water were greatest in the area adjacent to point sources, falling off rapidly in the far-field. Water and sediment criteria were not exceeded beyond Suncor or upstream of Polysar, indicating largely near-field contamination.

Sportfish (Channel Catfish and Carp) HCB levels in Lake St. Clair were typically in excess of the EPA fish consumption guideline (6.4 ng/g) in Lake St. Clair. It is worth noting that this criteria was developed based on an acceptable cancer risk of  $10^{-6}$  (1 in 1 million) while most standard-setting agencies including Health and Welfare Canada have adopted a risk level of  $10^{-5}$  (1 in 100,000). Consequently, the criteria may error conservatively; however, in view of documented positive carcinogenicity, this is likely warranted. This may be somewhat offset by the consumption level used in developing the guideline (6.5 g/day) not reflective of average Ontario angler and some Native people consumption levels (24.7 and 117 g/day respectively). A multi-stage model developed for use by the EPA permits the use of local consumption levels in place of average values, thus altering acceptable body burdens (EPA 1987). Consideration was given to these accurate consumption levels in development of load allocations (Section 6.6.2, Appendix 9). The Province of Ontario does not currently have an agency endorsed consumption guideline for HCB; however, one is under development.

FIGURE 5.3.3 DISTRIBUTION OF HEXACHLOROBENZENE IN WATER SEDIMENTS AND BIOMONITORS ALONG THE ONTARIO SHORELINE OF THE ST. CLAIR RIVER



While water and sediment guidelines were maintained in the far-field, biological organisms appear to be accumulating significant tissue levels.

(ii) Observed or Possible Effects

Acute lethality does not appear to pose a problem (Table 5.1.3) since  $LC_{50}$  values are typically greater than solubility. HCB exerts observable chronic, physiological responses (Table 5.1.3) at a much lower level and has been shown in separate studies to produce both positive and negative mutagenic responses. Chronic effects appear to be the driving force behind concerns over the occurrence of HCB in biological tissue.

A study by Niimi and Palazzo (1985) indicated that HCB was not eliminated by rainbow trout held at 4°C and that temperatures of 12°C were required to enable depuration. Rates were adjusted to factor out growth differences and thus compare on a common basis. This factor, coupled with other environmental variables all play roles in determining the concentration of HCB in biota.

According to Oliver and Niimi (1983), persistent organic contaminants such as HCB are largely taken up as food by higher trophic level organisms with more highly soluble contaminants accumulated from water. In the case of HCB, a long biological half-life, coupled with accumulation through the food chain has produced elevated concentrations in sculpins, juvenile fish and sport fish. Levels in sportfish were lower than sculpins or juvenile fish and may reflect time spent in Lake Huron and/or embayments of Lake St. Clair. It is likely that sportfish such as Carp would have proportionately higher body residues given residence in the St. Clair River only.

### (iii) Trends in the Receiving Environment

Improvements have been noted in HCB concentrations in a number of media in the last several years. The following table provides a brief summary of these results:

[HCB]	Water <sup>1</sup> (ng/L)	Sediments <sup>2</sup> (ng/g)	Juv. Fish <sup>3</sup> (ng/g)	Sportfish <sup>4</sup> (ng/g)
1983*		112	231	41.7
1984*	400			53.1
1985*	131	3280	69	49.0
1986	12	1349	25	26.6

<sup>1</sup> Samples obtained approximately 100m d/s of 1st St. Sewer complex

<sup>2</sup> Samples obtained approximately 600m d/s of 1st St. Sewer complex

<sup>3</sup> Samples obtained adjacent to Suncor from Spottail Shiners  
(Notropis Nudsonius)

<sup>4</sup> Channel Catfish (Ictalurus punctatus) from Lake St. Clair

\* 1983-85 data from (DOE/MOE 1986)

Significant reductions have been noted in water, and juvenile fish results. Sediments which are generally very heterogeneous, may be showing some improvements; however, this is a tenuous conclusion. Marginal improvements noted in Channel Catfish from Lake St. Clair may be tempered by their ranging habits.

#### 5.3.2 Hexachlorobutadiene

The distribution of HCBd is similar to that of HCB except that concentrations of the former are reduced in all but clams and juvenile fish. Figure 5.3.1 presents the mean and range of values measured in these compartments.

Loadings of HCBd from all sewers including the Cole drain measured during 1986-87 amounted to an average of 182.3 g/day. This compares to average HCB loadings of 20.7 g/day during the same period. While



whole effluent concentrations of HCBd were higher than HCB, it appears that the former is proportionately less bioavailable. This may be due to its lower  $K_{ow}$  resulting in a reduced affinity for lipids and other non-aqueous material. HCBd is also much more water soluble and volatile than HCB (Table 5.1.2). This is important in that the aqueous fraction is more available to be volatilized than a sediment-bound fraction.

Metabolism by means of contaminant induced enzymatic systems in higher organisms, e.g. Mixed-Function Oxidase (MFO) does not appear to play a role in reduced body burdens. Law and Addison (1981) found no differences in inducible enzyme activity between brook trout (Salvelinus fontinalis) exposed to hexachlorobutadiene and control animals.

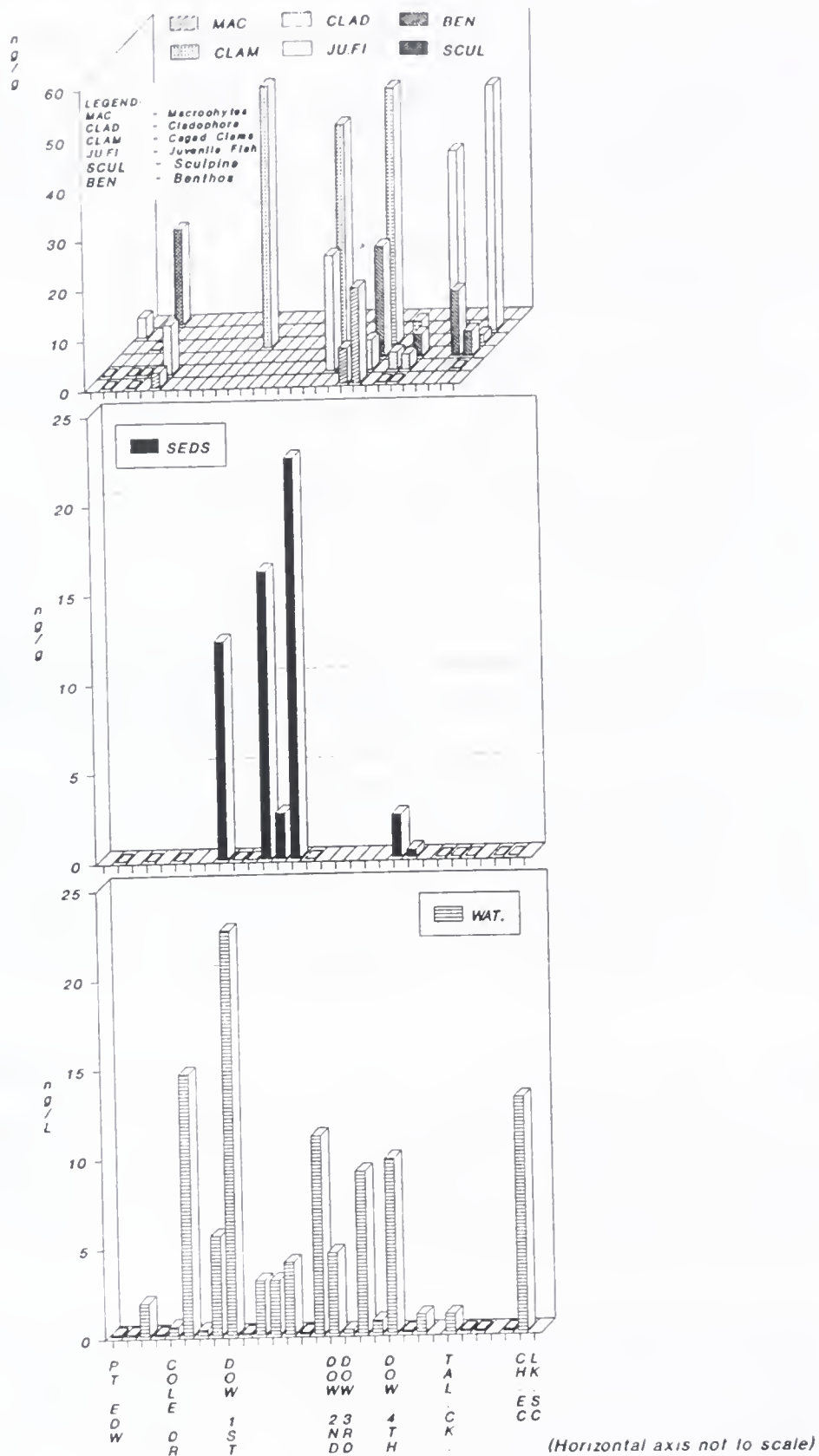
An examination of the relative mean concentrations between biota, provides evidence that higher trophic levels are more sensitive than aquatic vegetation. Juvenile fish contain tissue residues 60 and 90X greater than Cladophora and macrophytes respectively. The water solubility of HCBd is greater than 300 times that of HCB. This factor, coupled with a lower  $K_{ow}$  than for HCB results in decreased sediment associated concentrations relative to the dissolved fraction. Levels of HCBd measured in various media sampled during this investigation are presented in Figure 5.3.4.

HCBd criteria are available in water (0.1 ppb) and fish tissue (1.3 ppm) for the protection of aquatic life and piscivorous wildlife respectively. These levels have been established by agencies other than MOE (Table 5.3.1) and while not presently endorsed by the MOE, provide a basis for assessment.

The above guidelines were rarely exceeded in water (2 of 265 samples) and not exceeded in more than 100 biological samples (Table 5.3.1). The latter guideline has been developed by the New York State Department of Environmental Conservation for wildlife protection.



FIGURE 5.3.4 DISTRIBUTION OF HEXACHLOROBUTADIENE IN  
WATER SEDIMENTS AND BIOMONITORS ALONG THE ONTARIO  
SHORELINE OF THE ST. CLAIR RIVER



The U.S. EPA has established a Maximum Acceptable Toxicant Concentration (MATC) for HCB<sub>D</sub> in water of 9 ppb for pond snails. This level was 30 times greater than the highest observed HCB<sub>D</sub> concentration in water (300 ppt @ Station 203 during October 1986 sequential sampling). This MATC was exceeded in undiluted effluent on one occasion each at the Cole drain and Dow 42-inch sewer (Appendix 1).

It is apparent that acute lethality is not a concern based on the MATC and LC<sub>50</sub> values provided for several fish species in Table 5.1.3 (0.04 - 0.32 ppm).

As observed for HCB, environmental effects are typically of a chronic nature reflected in changes in the diversity of the benthic community as well as increased body burdens in biota. This is highlighted by an impaired benthic community adjacent to Dow and Poysar (Griffiths 1989).

Based on existing guidelines for the protection of aquatic life, HCB<sub>D</sub> appears to be a relatively minor concern. However, in the context of 182.3 g/day loadings to the St. Clair River, the assimilative capacity of the receiving environment must be considered.

A half-life of 3-300 days in water (Table 5.1.2) successively increasing from river, lake to groundwater has been observed. The relatively high vapour pressure and turbulence associated with a river environment account for a shorter half-life.

Investigative river sampling from 1986 indicates an increase in contaminant levels in bottom waters compared to surface waters.

It is likely that the greatest observed effects would be on benthic organisms in the St. Clair River and possibly in Lake St. Clair.

### 5.3.3 Octachlorostyrene

Relatively little is known about the behaviour of octachlorostyrene (OCS) in the environment. It was first identified in birds from the River Rhine in 1972. The first discovery in the Great Lakes occurred during 1976 at Saginaw Bay, and later at a number of locations in the lower Great Lakes (Kaminsky and Hites 1984).

OCS is produced from impurities in the manufacture of chlorine from electrolysis of a saturated sodium chloride solution (King 1987). Prior to the 1970's, this process employed graphite electrodes which were subject to decomposition, producing a waste "taffy" mixture of chlorinated organics, including HCB, HCB<sub>D</sub>, OCS and QCB. Since that time, a rather rapid and widespread conversion from graphite to metal electrodes has taken place with subsequent reductions in OCS production (Kaminsky and Hites 1984). Dow personnel have indicated a complete conversion to metal electrodes over the past several years. (R.W. Allen; Pers. Comm. 1989).

OCS is also produced as a by-product in industrial processes involving carbon and chlorine in high temperature reactions (Kuehl et al. 1981), such as carbon tetrachloride and tetrachloroethylene (King 1987) which are currently produced at Dow.

The occurrence of OCS in sediment cores obtained from Lake Ontario demonstrated an emergence in the early 1949's with a peak at or near 1970. These dates are consistent with advances in chlorine production and conversion to metal electrodes (Kaminsky and Hites 1984). Since the early 1970's, OCS levels have shown a dramatic decrease in Lake Ontario sediments consistent with the change in process.

Loadings of OCS from industrial sewers at Dow amounted to 4 grams/day. In excess of 9 grams/day were discharged from the Cole drain. The latter source is not a result of current manufacturing and likely reflects historical waste "taffy" deposited at Dow's Scott Road landfill site upstream of the Cole drain. It is difficult to determine what proportion of loadings from Dow outfalls represent current, process related or historical sources.

Both chlorine manufacturing plants at the Dow site discharge effluent to the 4th St. outfall. OCS loadings from this sewer; however, represent only 18% of the load discharged from the 42-inch sewer. This greater load may be attributed to incomplete process/waste water separation and/or historical surface on-site groundwater contamination.

Dow is currently making significant efforts to isolate the contaminated fraction and treat as required.

(i) Comparison with Guidelines

The Ministry of the Environment has established a tentative advisory of 0.1 ppt for OCS. New York State has developed a fish flesh criteria of 0.02 ppm for the protection of piscivorous wildlife. Even though this latter value may be less stringent than a human health criteria as demonstrated for HCB, there remain 69% of biological organisms in the near-field and 40% at far-field stations at levels beyond this criterion.

The MOE water quality advisory is very conservative since it is based on limited toxicological information. Since it is below analytical detection limits (1 ng/L), any detected values will exceed this advisory. Measured OCS concentrations in water and sediments are presented below:

	WATER <sup>1</sup>		SEDIMENTS <sup>2</sup>	
	A	B	A	B
MEAN	0.5	0.01	1557	2.8
MIN	0	0	0	0
MAX	20	1	5600	10

<sup>1</sup> - Data from investigative sampling component (ng/L).

<sup>2</sup> - Data from sediment and In-place pollutants surveys (ng/g).

A - Area between Polysar (Sarnia) and Suncor.

B - Remainder of St. Clair River (upstream of Polysar and downstream of Suncor).

It is apparent that OCS is highly bioaccumulative, given that loadings from Dow and the Cole drain are fairly minimal (13 g/day) and 40% of all biological samples exposed/collected outside of the Polysar to Suncor vicinity exceeded the 0.02 ppm guideline.

#### (ii) Trends in the Receiving Environment

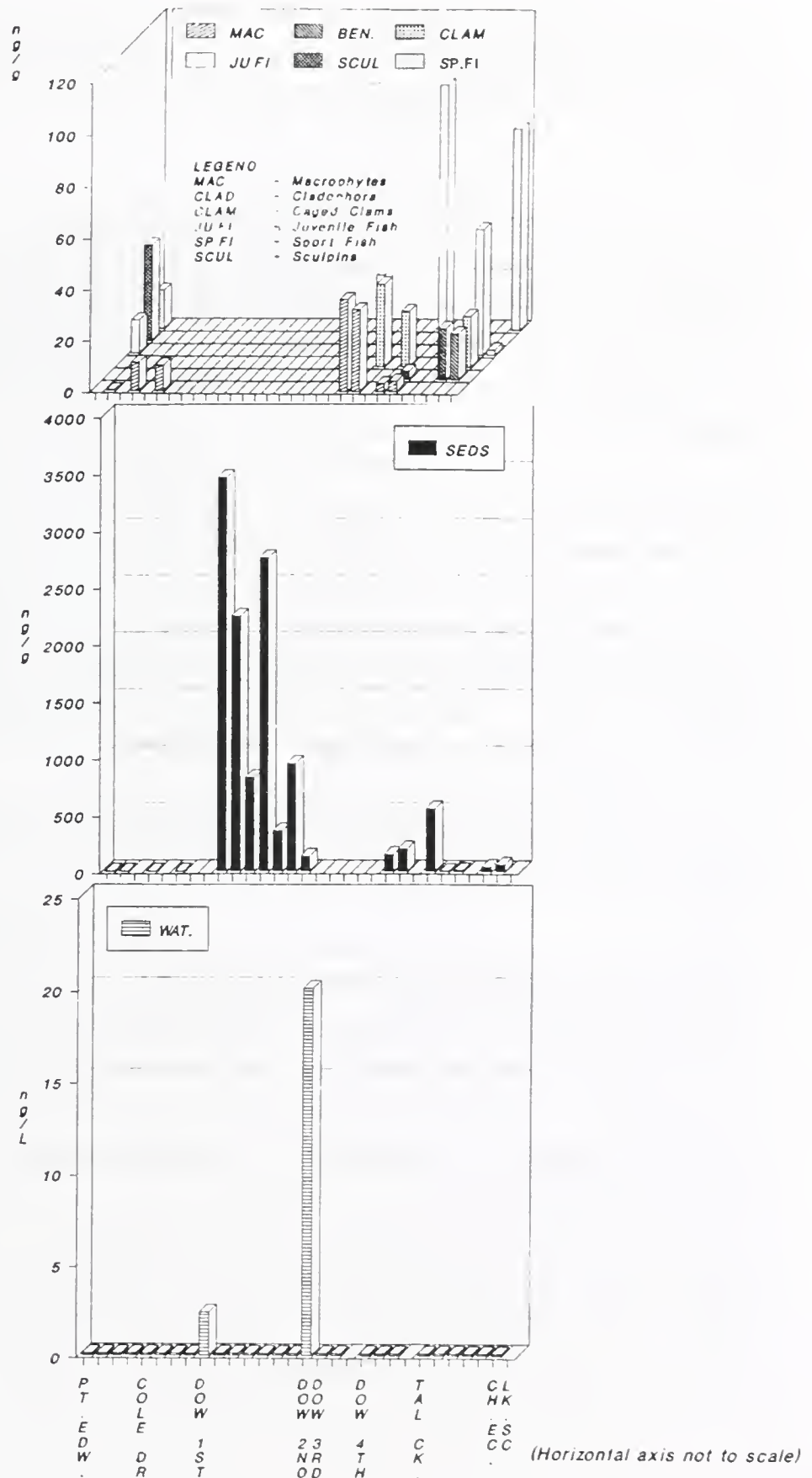
Talfourd Creek has been identified as a minor contributor of OCS to the St. Clair River; however, the source remains to be documented. Instantaneous loadings extrapolated to daily loadings measured at the mouth of Talfourd Creek (Johnson and Kauss 1989) amounted to approximately 0.3 grams/day during a study conducted in 1984 and 1985.

No additional sources have been identified in the St. Clair River watershed. The significance of airborne loadings and contributions from Talfourd Creek require further evaluation.

Figure 5.3.5 provides a summary of the distribution of OCS in various biological media, as well as water and bottom sediments.

Values reported for clams, juvenile fish and sport fish are per unit wet weight. All others are reported on a dry weight basis. Studies by Kauss and Hamdy (1985) and Suns (1989 pers. comm.) indicate

FIGURE 5.3.5 : DISTRIBUTION OF OCTACHLOROSTYRENE IN WATER SEDIMENTS AND BIOMONITORS ALONG THE ONTARIO SHORELINE OF THE ST. CLAIR RIVER



approximately 80% to 85% water content in clams (Elliptio complanata) and juvenile fish, thus requiring that wet weight contaminant levels be multiplied by a factor of 5-7 in order to compare with dry weight measurements.

Caution must be exercised in standardizing results in this manner, particularly with respect to sportfish, which may require consideration of differences between species and their habitats. A further correction factor must be applied to sportfish since results are reported for edible portions only (fillets) and not whole fish homogenates.

To avoid additional error which may result from these conversions, a relative comparison of reported values has been undertaken.

Juvenile fish, sculpins and sportfish obtained in the vicinity of Point Edward all contained OCS concentrations between 13 and 40 ng/g (ppb) (wet weight). This may represent uptake of contaminants and subsequent migration of the animal to a "clean" area.

Macrophytes near the Cole drain contained low levels from that source, possibly reflecting some backeddy effects at the upstream station.

Sediments were not collected near the Cole drain during 1986; however, samples obtained in 1983 (DOE/MOE 1986) indicated levels approaching 10000 ng/g (10 ppm). Environment Canada reported values of up to 6 ppm during 1985 (DOE/MOE 1986) near the Cole drain outfall but only 10m from shore. This may more accurately reflect historical contamination prior to installation of an extended (68m) submerged diffuser installed in 1982.

Peak sediment concentrations in 1986 were observed adjacent to the Dow 1st St. complex 10m off-shore (max 5600 ng/g - 5.6 ppm; mean 3455 ng/g) with progressively decreasing concentrations toward the Dow 2nd St. sewer.



Sediment OCS levels appeared to increase somewhat from downstream of Talfourd Creek to Chenal Ecarte. This may be coincident with a higher proportion of clay found in sediments at both these locations (see Figure 4.2.5b).

OCS was rarely detected in water samples (see Section 4.2.2). A maximum value of 20 ng/L (ppt) was recorded at Station 209 adjacent to the Dow 2nd St. outfall. A sample containing 17 ppt OCS was collected downstream of the Cole drain 100m off-shore; however, this is not indicated in Figure 5.3.4 as only near-shore results are plotted. Both samples were collected in July coincident with high ambient water temperatures and solubility.

Biological samples were generally unavailable adjacent to Dow and Polysar. Introduced clams yielded, some information; however, recovery of cages was low and some analytical difficulties were encountered. Concentrations were highest near the Dow outfalls and declined only marginally with distance downstream.

Sculpins and sportfish had increasing body burdens with maxima observed in the lower river and Lake St. Clair respectively.

#### 5.3.4 Tetrachloroethylene

The 1985 intensive investigation of the St. Clair River was prompted as a result of a spill of tetrachloroethylene (PERC) to the St. Clair River by Dow Chemical.

This material happens to be a principal product in the Dow operation; however, technically it is a by-product in the chlorinolysis reaction of hydrocarbon feedstock with excess chlorine under severe conditions (King 1987). As a result of this process, another end-product, carbon tetrachloride, is manufactured. Additional by-products, which result include some highly chlorinated compounds as well as some heavy tars containing HCB, HCBD and OCS (King 1987).

PERC differs from these compounds for a number of chemical characteristics. It is much more soluble (150 ppm) with a correspondingly low log  $K_{ow}$  of 2.6. It has a much higher vapour pressure (volatility) than HCB, HCBd or OCS and a brief half-life in water and tissue (see Table 5.1.2).

(i) Comparison with Guidelines

A number of guidelines/advisories exist for PERC, which have been developed for the protection of human health. These are typically in the range of 2-10  $\mu\text{g/L}$ . The World Health Organization (WHO) and the U.S. EPA have established values of 10 and 8  $\mu\text{g/L}$  respectively which correspond to a cancer risk of 1 in  $10^5$  (Wells 1985).

The more restrictive guideline was exceeded by only 7% of ambient water samples collected in the Polysar to Suncor vicinity and 0% upstream and downstream.

A criterion of 260 ppb has been established by the CCREM (1987) for the protection of aquatic life. This value was not exceeded during 1986 sampling (max = 44 ppb adjacent to Dow 1st St. complex); however, a single exceedence was observed during 1985 (DOE/MOE 1986; 1120  $\mu\text{g/L}$ ).

PERC levels at the southern Suncor property line during 1985 routinely exceeded the 8 ppb guideline, while concentrations measured in 1986 averaged <1 ppb from the same location.

Due to the volatile nature of PERC, and its brief half-life, it does not readily accumulate in biological tissues or sediments and is difficult to accurately quantify through chemical analysis. While attempts were made to measure PERC in these media, no jurisdictional guidelines were available as a basis for comparison. Figure 5.3.6 presents data on tetrachloroethylene for water, sediments, clams and juvenile fish.

(ii) Observed or Possible Effects

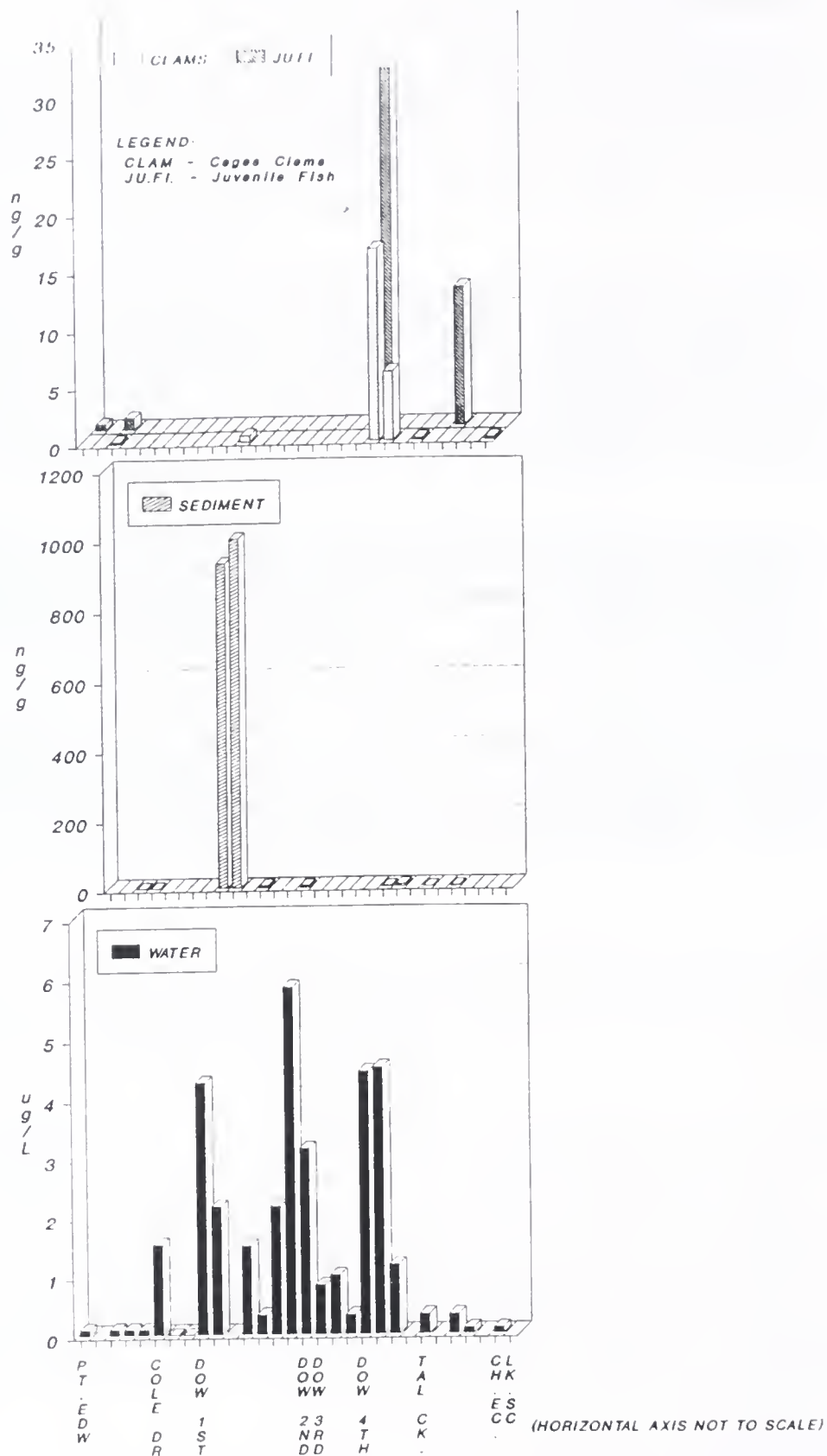
Tetrachloroethylene tends to form globules in the water column and sink to the bottom in puddles. Subsequent to the 1985 spill by Dow, a 46m x 50m clean-up zone was identified from which approximately 700m<sup>3</sup> of contaminated sediment was removed (Rodgers 1986).

Benthic invertebrate communities extending 100m downstream of the 1st St. outfalls reflected impaired water and sediment quality through reduced abundance and the absence of certain species (Section 4.4.6). Diver observations during this time also indicated a reduction in the number and variety of benthic organisms including sculpins.

These observations are corroborated by sediment toxicity results which indicate mean mortalities of 33% for fathead minnows (Pimphales prometas) and 87% for mayflies (Hexagenia limbata) exposed to sediments collected from this vicinity (Section 4.3.2).

While these findings cannot be attributed directly to the occurrence of PERC in the sediments, it is the primary constituent of the puddle material comprising at least 60% (DOE/MOE 1986).

FIGURE 5.3.6 DISTRIBUTION OF TETRACHLOROETHYLENE  
IN WATER SEDIMENTS AND BIOMONITORS ALONG THE  
ONTARIO SHORELINE OF THE ST. CLAIR RIVER



## 6.0 ST. CLAIR RIVER LOAD ALLOCATION

### 6.1 Purpose

The purpose of this section is to outline a procedure for the allocation of effluent loads to meet water quality guidelines.

### 6.2 Introduction

The following addresses the problem of load allocation at multiple outfalls. The exposure models predict the two dimensional pattern of concentrations throughout the receiving waters. In order to apply the models to load allocation it is first necessary to establish water quality objectives; then it must be determined where in the receiving waters these objectives are to be met. Moreover since the inputs are highly random, a statistical compliance criteria or a level of compliance should be set e.g. the objective should not be exceeded more than 5% of the time on a monthly averaged basis outside of a relatively small mixing zone (MZ - see Section 6.3). The six outfalls shown in Table 6.2.1 were selected for detailed treatment.

Although the samples were analyzed for some 63 compounds, most of these were present at concentrations at or below the detection level and thus were unsuitable for model calibration. In the final analysis the following contaminants were selected for model development:

HCB - Hexachlorobenzene [ $\text{LOG } K_{ow} = 5.5$ ; Range 5.2 - 6.4]

HCBD - Hexachlorobutadiene [ $\text{LOG } K_{ow} = 4.78 - 4.9$ ]

HCE - Hexachloroethane [ $\text{LOG } K_{ow} = 3.58$ ]

PERC - Tetrachloroethylene [ $\text{LOG } K_{ow} = 2.6 - 2.88$ ]

CCL4 - Carbon tetrachloride [ $\text{LOG } K_{ow} = 2.64$ ].

OCS - Octachlorostyrene [ $\text{LOG } K_{ow} = 6.29$ ]

2,4,5 - TCT - 2,4,5 - Trichlorotoluene [ $\text{LOG } K_{ow} = 4.72$ ]

TABLE 6.2.1: MIXING ZONE DEFINITION

Outfalls	Djet (in)	Depth (ft)	Discharge (cfs)	$X_1$ (ft)	$X$ (ft)	$C_m H$	$X_c$ (ft)
Cole drain	72	25+	29	0	1700	100	100
Polysar 72"	72	20+	11.2	1700	890	100	100
Dow 1st Street 42"	42	20+	60	2590	977	100	100
Dow 2nd Street	36	20+	22.0	3467	963	100	100
Dow 3rd Street	36	20+	30.5	4330	870	100	100
Dow 4th Street	72	20+	148	5200	1000	100	100

$C_m$  - 5

$X_c$  - is the lesser of  $X$  and  $C_m H$

$X_1$  - distance downstream from the Cole drain

$X$  - distance downstream to next outfall or intake

### 6.2.1 Description of Models Used

#### (a) The KETOX Model

The KETOX model consists of two components namely, the hydrodynamic and the dispersion subprogramme and the mass transport and fate subprogramme. The programme produces a steady state (not varying with time) solution for the depth-averaged velocities, lateral dispersion coefficients, concentrations of contaminants in the water column, the suspended sediments, the bed sediments, and the response time constants to achieve equilibrium. The input data consists of: river flows, river cross-sections, Mannings "n" (U.S. Corps. of Engineers use "n" to represent the bed friction; a typical value of "n" for the connecting channels of the Great Lakes is in the range 0.023 to 0.026), depth corrections from low river stage, initial velocity distribution, diversions and inflows, outfall loadings and location, kinetic data for the contaminants, partitioning coefficients, concentrations of suspended solids, concentration of solids in the bed, active bed layer thickness, and initial concentration of the contaminant.

The theory for the hydrodynamic components of the model are given in the Users Manual for KETOX (Appendix 7). The theory for the partitioning to the solids and active bed interaction is based on Ditoro et al. (1982, 1984). The model includes chemical loss due to volatilization, photolysis, hydrolysis, oxidation and biodegradation. The modelling procedure for treatment of these terms was taken from Thomann and Mueller (1987).

The model simulation for the load allocation procedure started just upstream of the Cole drain and extended to Stag Island along the Canadian shoreline. Since the whole river model predicted that the contaminants remain within the Canadian portion of the river upstream of Stag Island only this portion of the river was included in the load allocation procedure. The whole river model was used for all other simulations.



Figure 6.2.1 shows the reaches that were used to represent the changing hydraulic characteristics of the whole river. Each of the reaches is divided into 14 stream tubes with assigned fractions of the total channel flow. Figure 6.2.2 shows the system diagram for the study reaches. Briefly, reaches marked "Dispers" are subject to moderate lateral mixing as estimated by the K-E turbulence model (Rastogi and Rodi 1978, Rodi 1980). Reaches marked "uniform" are those that produce complete or nearly complete mixing. Reaches marked "Comb" involve the confluence of two flows and the associated mixing. The programme also has the capability of diverting flow to other channels or around islands via a subroutine "Split". The programme is controlled by a directory file (see example in Users Guide) which calls, in a logical sequence, the appropriate subprogrammes. The river and contaminant data are given on a separate file an example of which has been given in the Users Guide (Appendix 7). An extract of the programme output is also included in the Users Guide for the model.

Figure 6.2.3 shows the refined grid that was used from the Cole drain to Stag Island. The grid size for this zone was 40 ft in the longitudinal direction and approximately 30 ft in the transverse direction. Fourteen flow panels were used to represent the 22% of the river flow nearest the Canadian shoreline.

(i) Sensitivity Analysis - KETOX Model

A sensitivity analysis was carried out for this model within the context of the St Clair River. A sensitivity analysis is performed by perturbing one of the input parameters in the model and recording the change in the output of the model. Such an analysis is useful in understanding the processes that the model is intended to simulate. The information obtained can help in the planning of future data collection as well as in the calibration of the model.

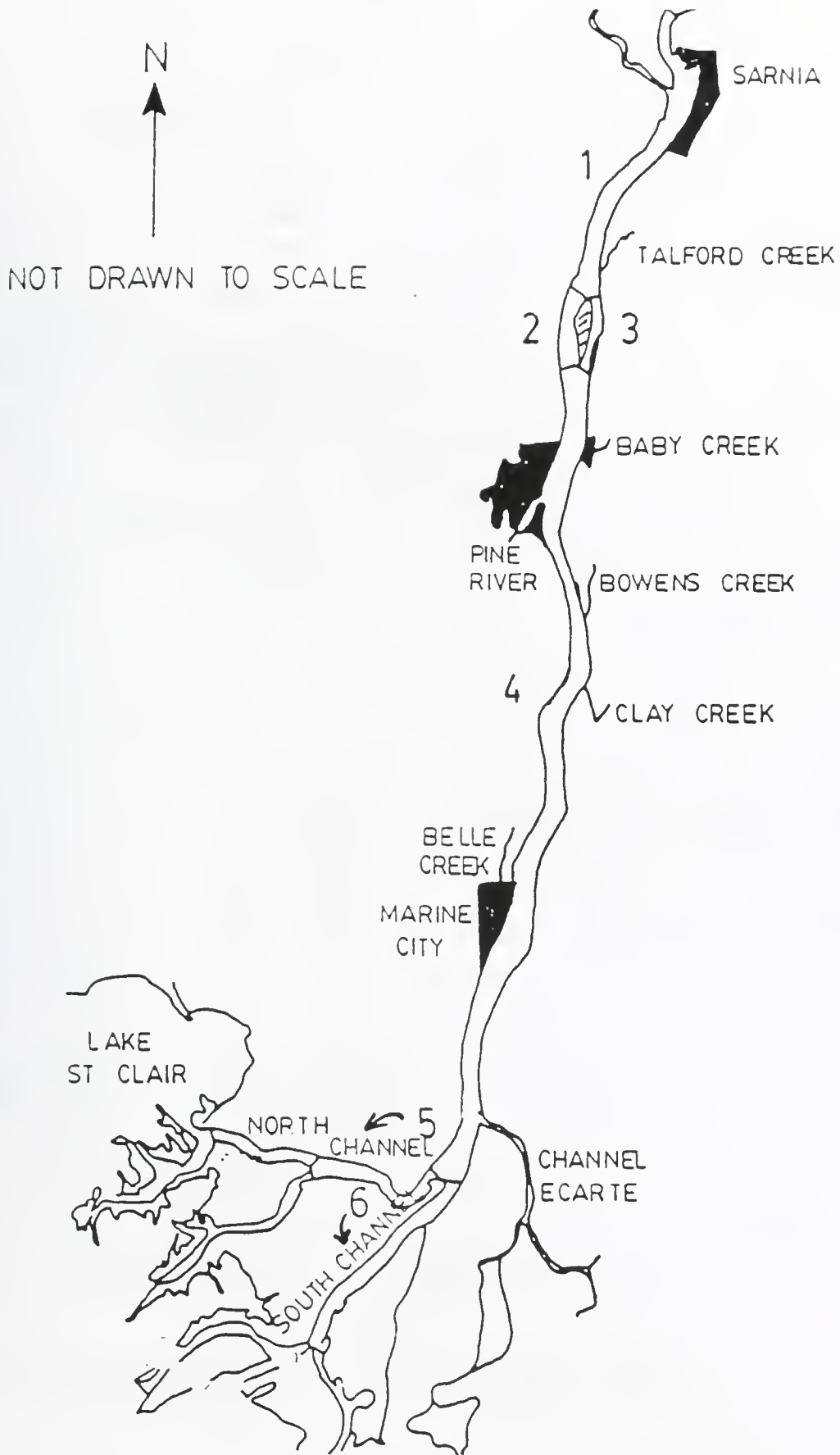


FIGURE 6.2.1: Definition of Reaches for the KETOX Model for the St. Clair River

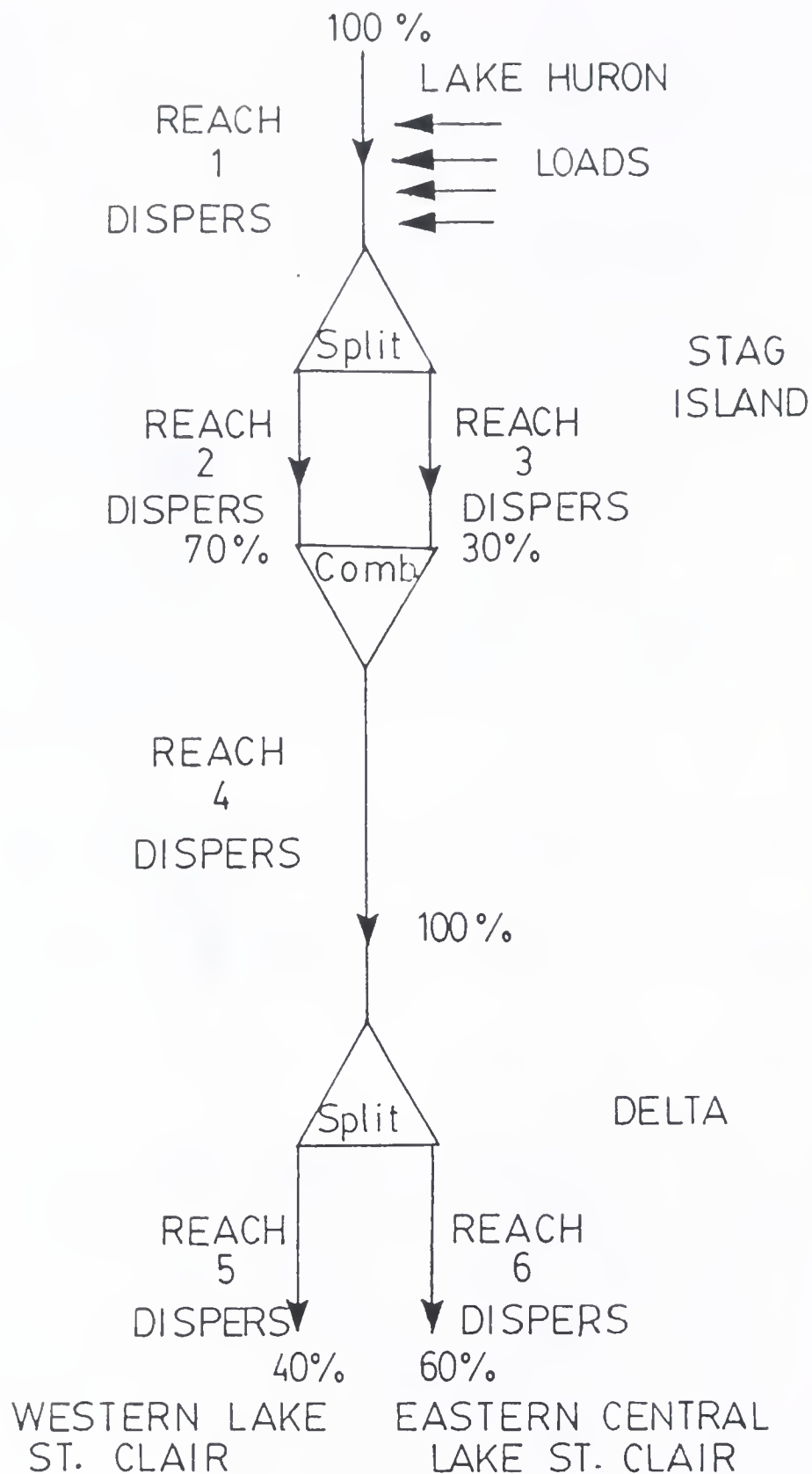


FIGURE 6.2.2: Schematic of the St. Clair River for the KETOX model

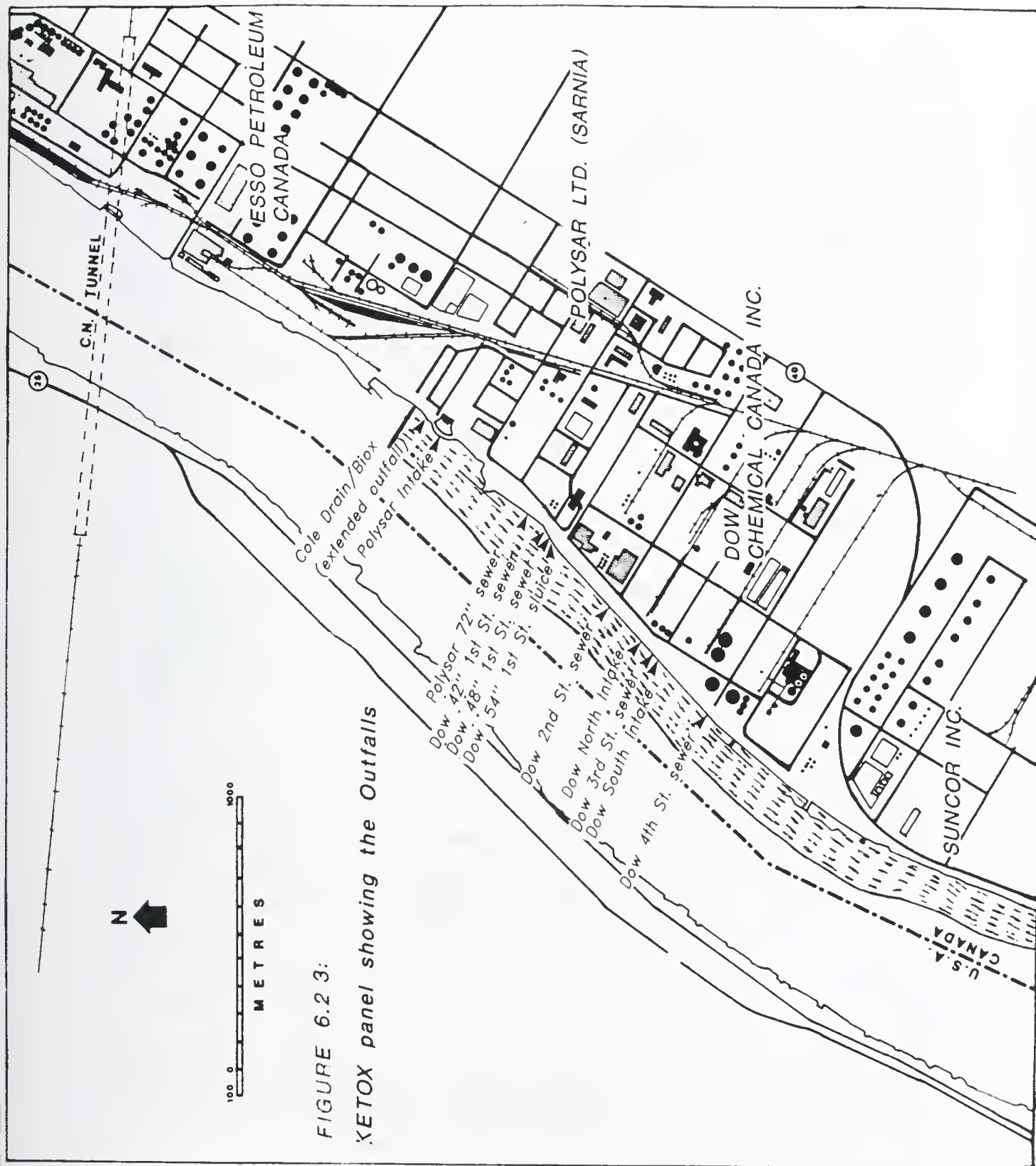


FIGURE 6.2 3:  
XETOX panel showing the Outfalls

Sensitivity analyses were made for the following parameters:

- a) contaminant load,
- b) dispersion coefficient,
- c) river flow,
- d) contaminant  $K_{OW}$ ,
- e) partition coefficient,
- f) suspended solids,
- g) active bed layer thickness,
- h) pore water diffusion,
- i) decay rates in the bed,
- j) settling and resuspension rates,
- k) volatilization rates.

A brief summary of the results are presented here.

As expected from the fact that the governing transport equations are linear, the exposure concentrations at a given point in the receiving waters show a linear response to the input loads. Several of the load response curves are given in section 6.6 on load allocation.

The effect of the lateral dispersion coefficient on the exposure concentrations increases with the distance from the source. Within the initial mixing zone, 5 to 10 pipe diameters from the outfall, the momentum of the effluent jet dominates. Beyond this zone the turbulent dispersion of the river rapidly becomes the controlling factor in the dilution process. The following example illustrates the response of the model to a 2/3 change in the lateral dispersion coefficient. A unit load of HCBd was applied at the Dow 1st Street sewer complex while the model was run for the base value of the dispersion coefficient (mean value approximately  $0.25 \text{ m}^2/\text{s}$ ) and then all of the computed dispersion coefficients were increased by 2/3 and the run was repeated. Figure 6.2.4 shows the normalized total concentration profile at Stag Island for the base and the increased dispersion. The normalizing concentration  $C_0$  is the shoreline

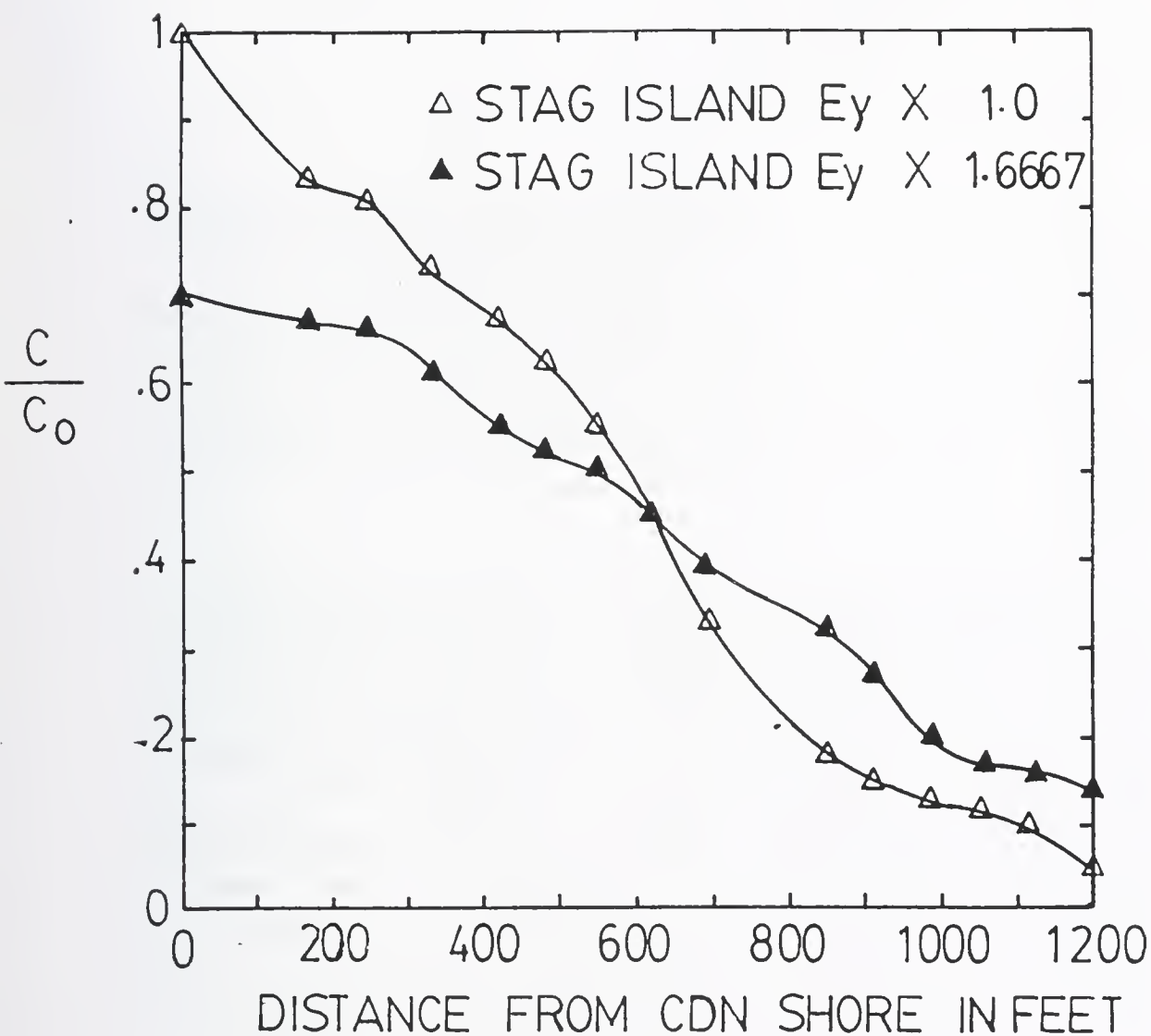


FIGURE 6.2.4: Effect of Lateral Dispersion on Concentration Profile at Stag Island

concentration for the base dispersion values. It is noted that in a distance along the river of about 7000m the 2/3 increase in dispersion coefficients resulted in a 30 percent decrease in the shoreline concentration with the consequent spreading of the plume. This analysis indicates the importance of lateral dispersion in the model calibration process.

The river flow was varied from 140,000 to 230,000 cfs with all other inputs held constant. Figure 6.2.5 shows the water column concentration near the downstream boundary of the Mixing Zone (MZ) for the Dow 1st Street sewer complex for the range of river flows tested. It is noted that the concentration is inversely proportional to the river flow. This analysis also indicated that the plume width, near the source, slightly decreases with increasing river flow.

Since contaminant partitioning is usually correlated with  $K_{OW}$  and since the effect of partitioning depends on the concentration of suspended solids, these three factors were analyzed as a group. One of the main effects of sorption of contaminants to particulates is the change in the fraction of dissolved to total contaminant in the water column. Figure 6.2.6 shows the variation of the ratio  $C_d / C_T$  for partition coefficient ranging from  $10^3$  to  $10^8$  L/Kg. Suspended solids were varied from zero to 8 mg/L. It is noted that for contaminants with partition coefficients less than about  $10^4$ , it is reasonable to assume that all the chemical is in a dissolved or bioavailable form. Thus in this study HCB, HCE, PERC and CCL4 can be considered to be primarily dissolved while HCB and OCS would be affected by suspended solids.

The thickness of the sediment active bed in the river depends on several factors including the height of ripples and dunes and bioturbation depth. Alluvial deposits in the river bed vary in thickness from less than 1 cm to about 40 cm. The bed material in these deposits consists of gravel, sand, silt and organic matter. These deposits are generally underlain by clay (see Section 2.1). The



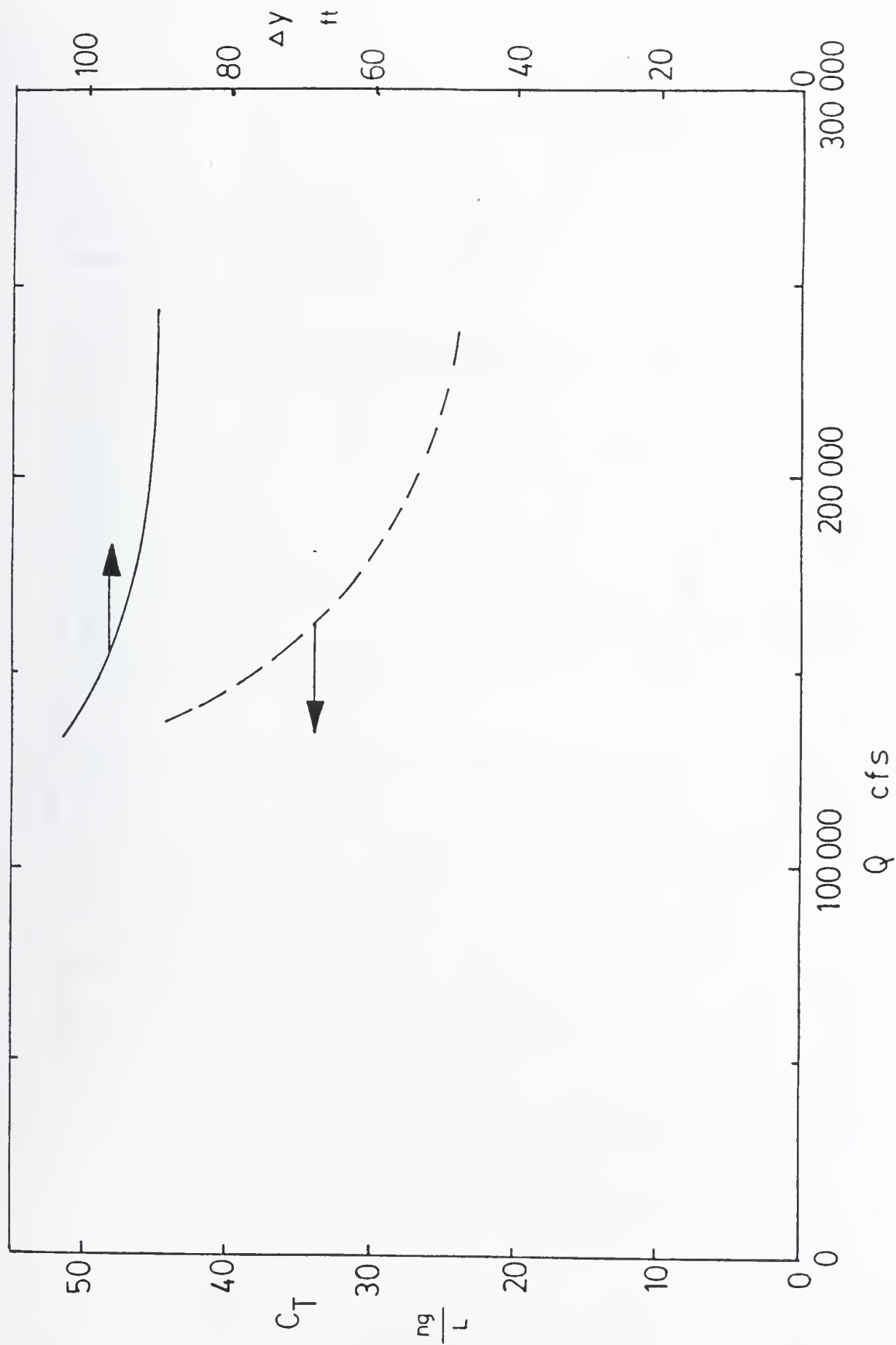


FIGURE 6.2.5: Effect of River Flow on Ambient Concentrations and Plume Width

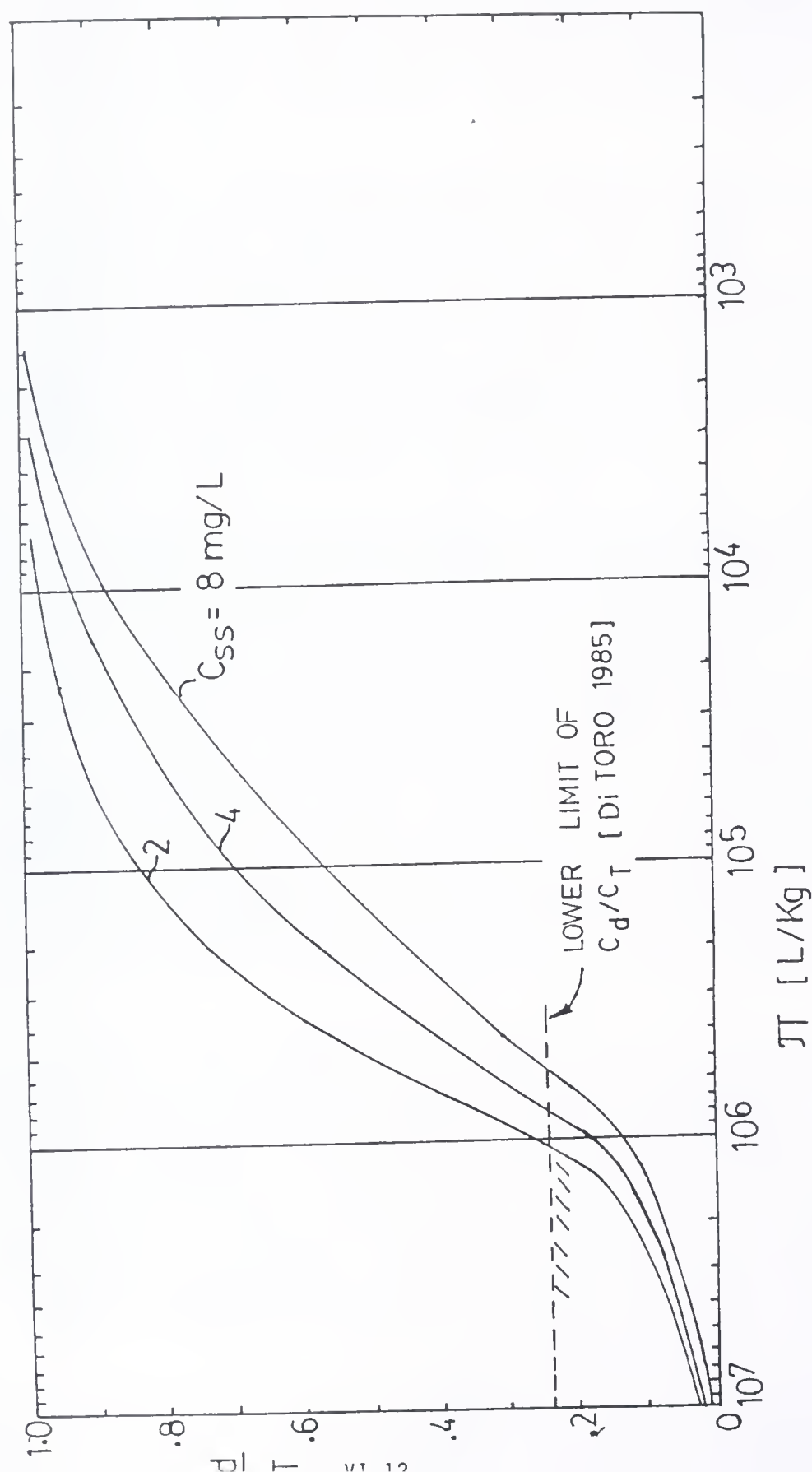


FIGURE 6.2.6: The Effect of Partition Coefficient and Suspended Solids on Dissolved Fraction

bed response time in KETOX is measured by the  $t_{1/2}$  which is the time required to achieve half of the equilibrium concentration assuming a zero bed concentration at time zero. Figure 6.2.7 shows the relationship between bed thickness and  $t_{1/2}$  for a decay constant of  $10^{-7} \text{ L/s}^{-1}$  for HCB near the source. For a bed thickness of 30 cm which is typical of the Dow site the  $t_{1/2}$  is of the order of 0.2 years; the corresponding  $t_{1/2}$  near the river Delta under the same conditions is of the order of 1 year.

Pore water diffusion was increased by 2 orders of magnitude and found to cause only a 50 percent reduction in the  $t_{1/2}$  as illustrated in Figure 6.2.8. Figure 6.2.8 also shows that increasing the diffusion coefficient increases the concentration of contaminant sorbed to the bed sediment. When diffusion is high, the concentrations on the suspended solids and the bed sediments are more likely to be similar. The molecular diffusion is extremely small; however, the effective diffusion may be significant in some cases, such as when there is highly turbulent flow over a gravel bed; or when bioturbation is high; or when there is bulk movement of pore water; or when immiscible contaminants are spilled on the bed.

The decay rate constant for the contaminant in the bed is a highly uncertain factor in the model. A base value of  $10^{-7} \text{ L/s}$  was assumed for HCB based the minimum expected loss rates in the water column. For the sensitivity analysis this value was varied from  $10^{-8}$  to  $10^{-6} \text{ L/s}$ . Figure 6.2.9 shows the effect of decay rate on the  $t_{1/2}$ . It is evident that the decay rate is a major governing factor in the determination of the bed response. Figure 6.2.10 shows that the ratio of contaminant concentration on the bed sediment to contaminant on the suspended sediments is nearly 1 at the lowest decay rate and decreases significantly as the decay rate increases. The observed persistence of high contaminant levels near the Dow site for several months after the 1985 PERC spill seems to support the use of a low decay rate in the bed; a value in the range  $10^{-8}$  to  $10^{-7} \text{ 1/s}$  is suggested.

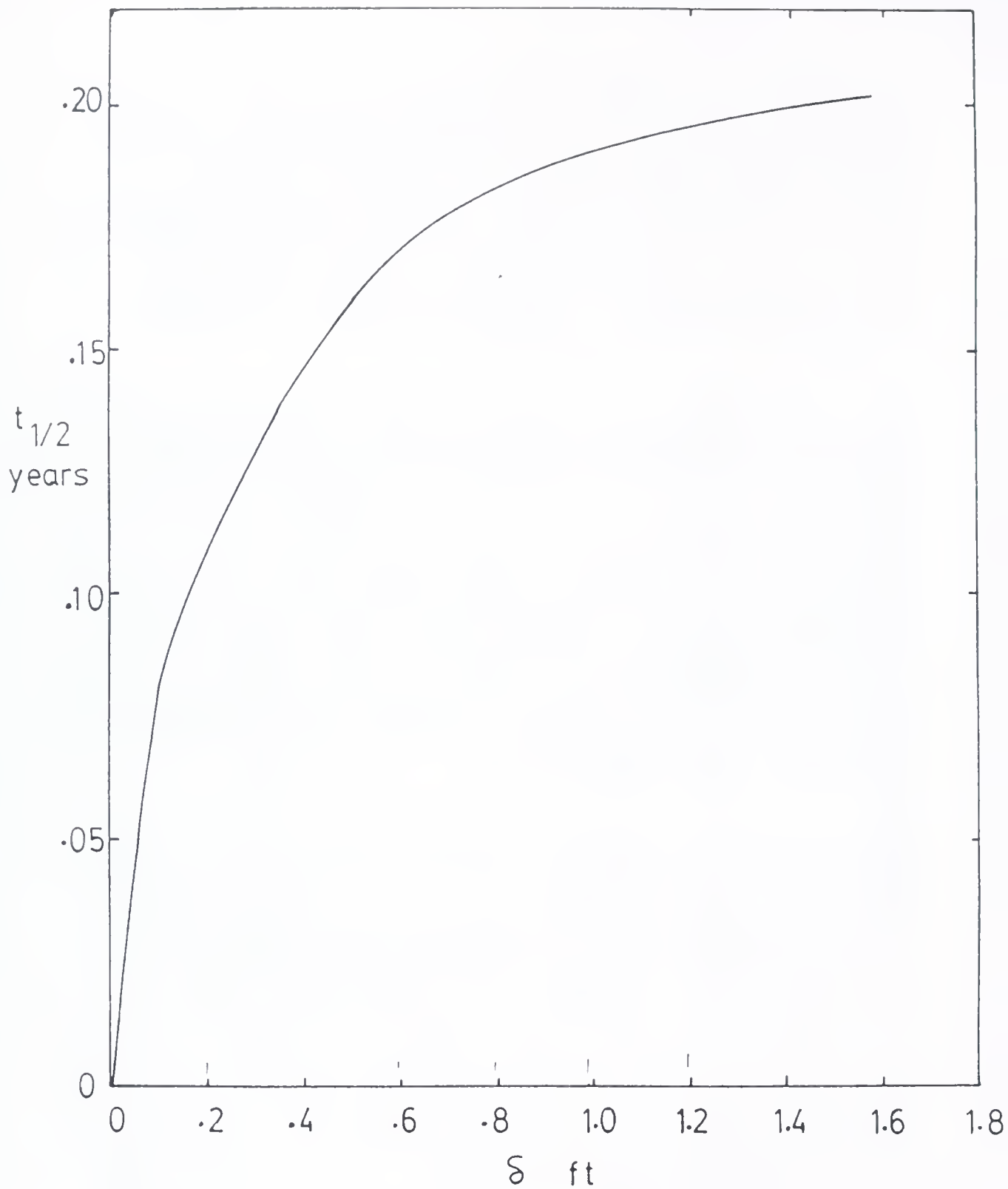


FIGURE 6.2.7: *Effect of Active Bed Thickness on Bed Response Time for HCB with Bed Decay Rate of  $10 \rightarrow 1/s$*

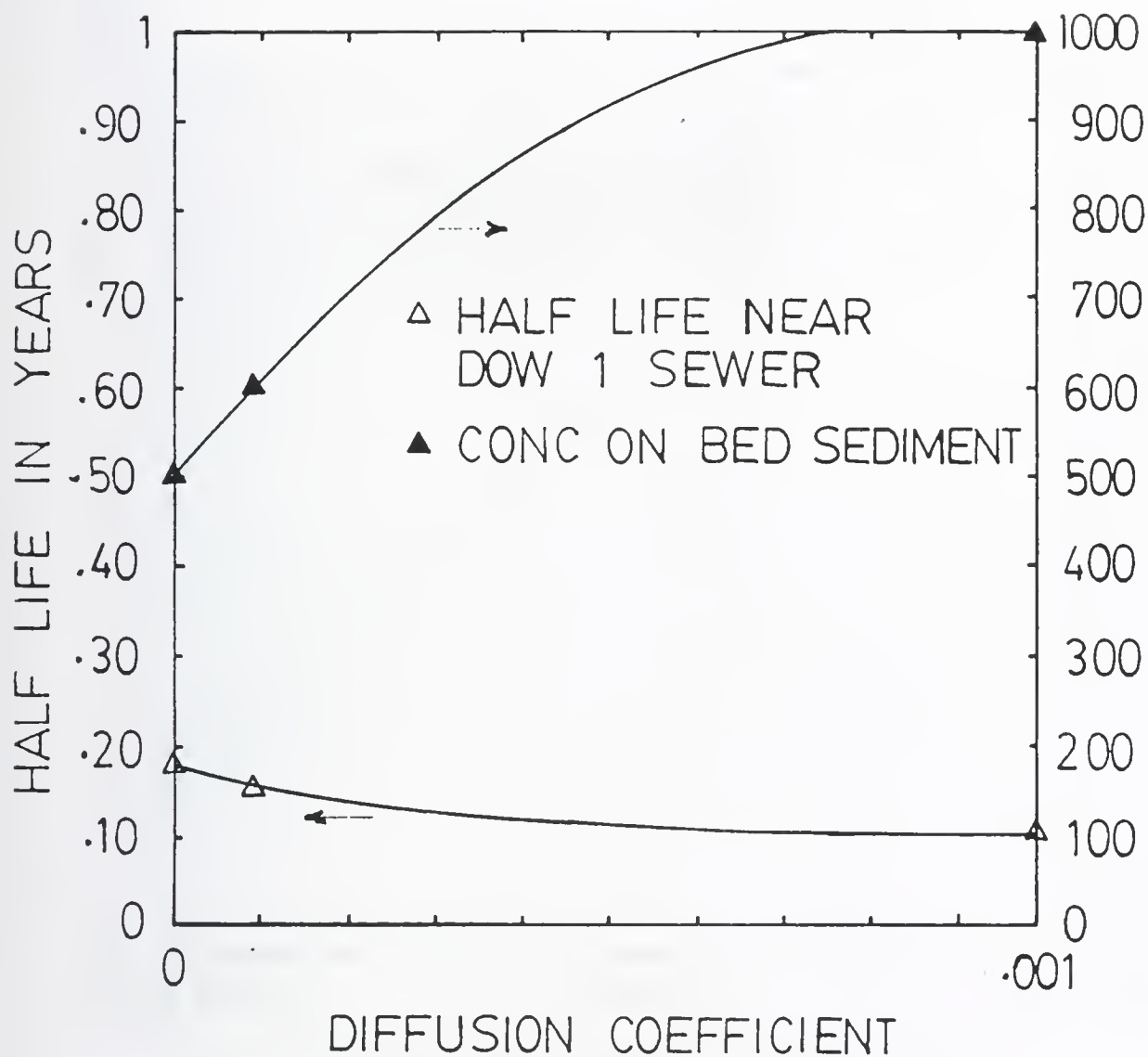


FIGURE 6.2.8: Effect of Bed Diffusion Processes on the Bed Response for HCB

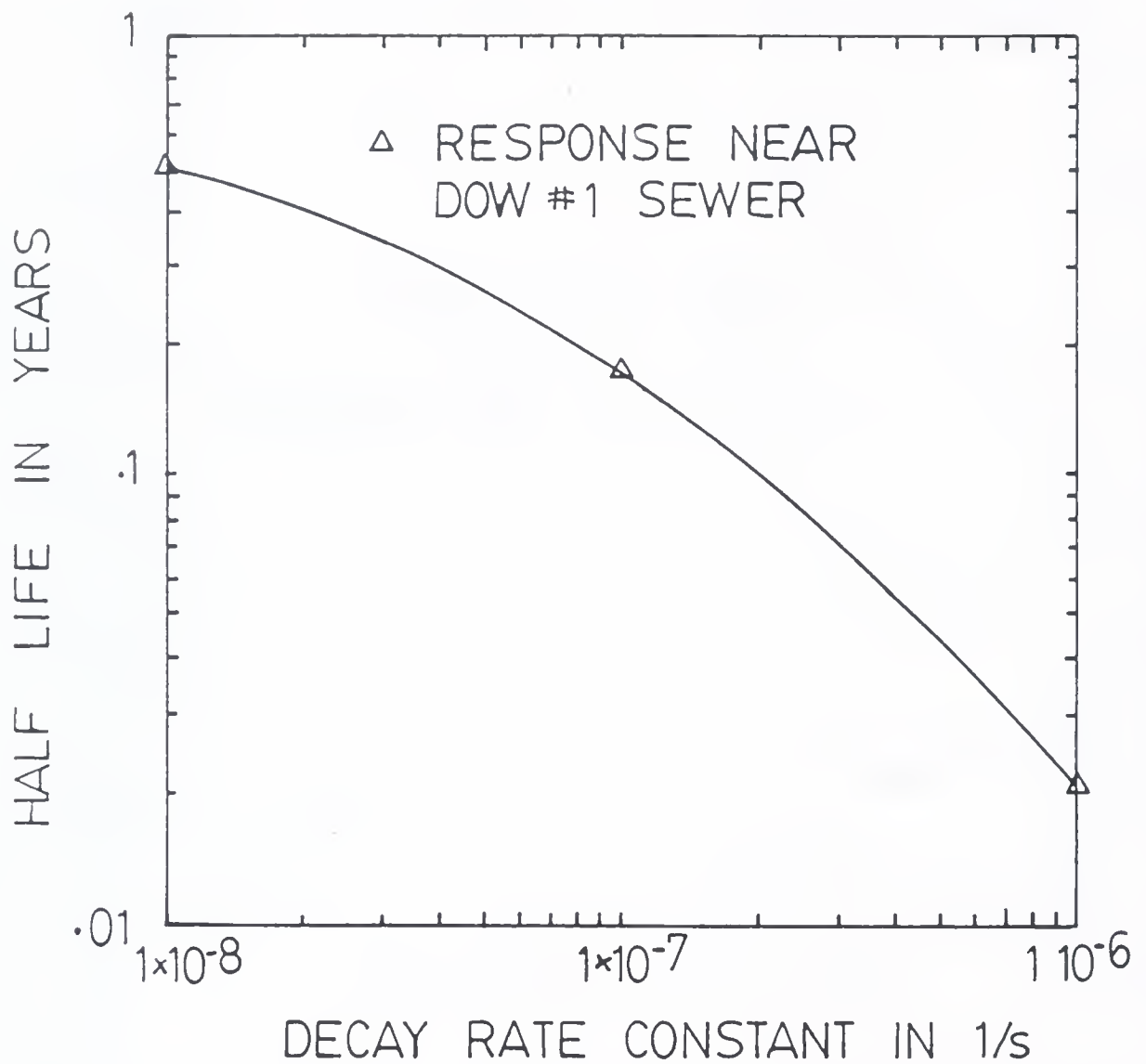


FIGURE 6.2.9: Effect of Decay Rate on Bed Response for HCBd

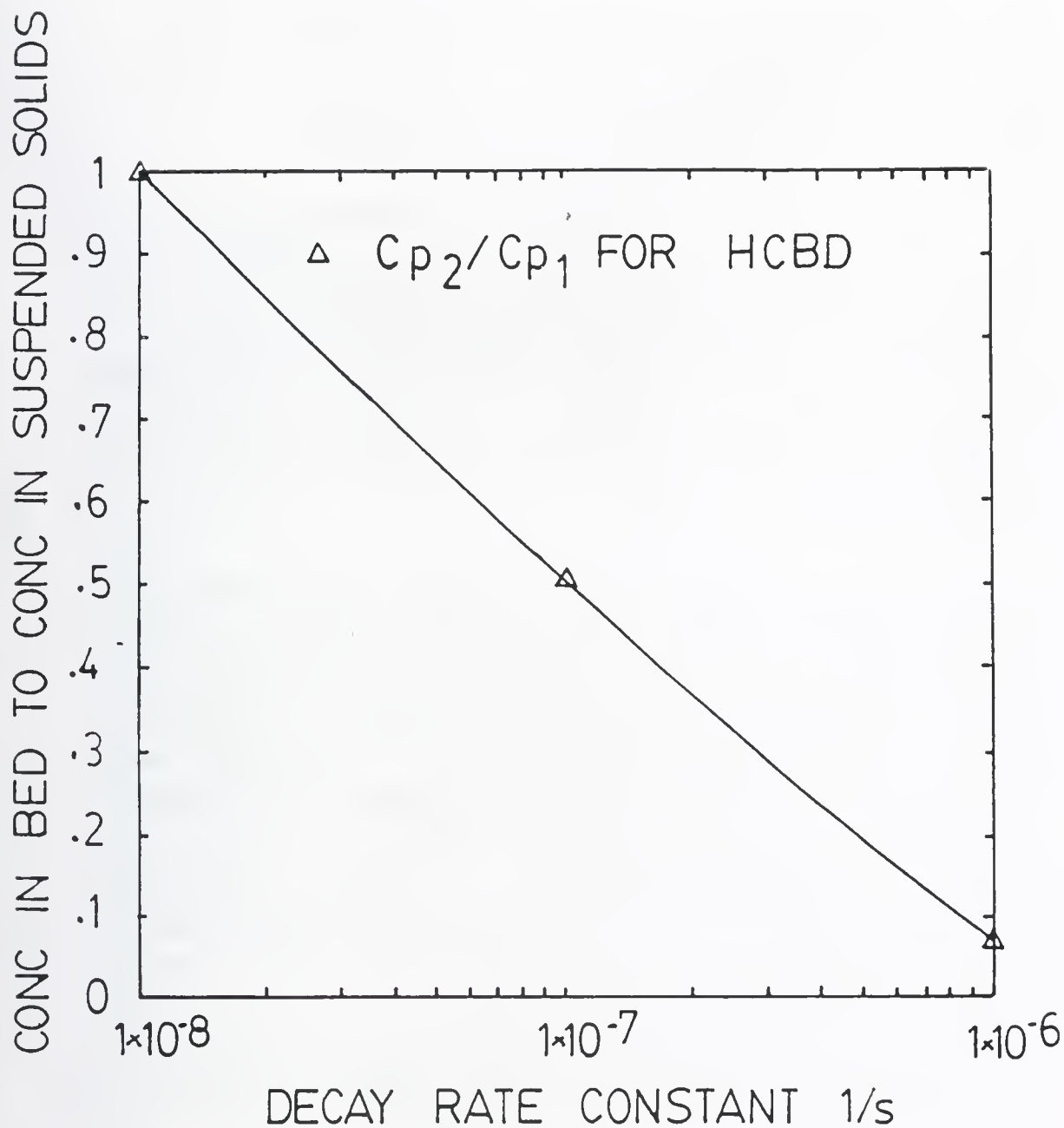


FIGURE 6.2.10: Effect of Bed Decay Rate on the Ratio of Bed Contaminants to Concentration on Suspended Solids



There is no documented net sedimentation occurring upstream of the Delta in the St. Clair River. Under these conditions there is a dynamic equilibrium between the sediments settling out of the water column and those being resuspended, i.e. on the average  $C_{SS} * V_{SS} = C_{SBED} * V_{RS}$ , in which  $C_{SS}$  = concentration of suspended solids;  $V_{SS}$  = settling velocity of suspended solids;  $C_{SBED}$  = concentration of solids in the bed;  $V_{RS}$  = resuspension velocity. The effect of sediment movement was studied by varying both  $V_{SS}$  and  $V_{RS}$  by the same factor. As indicated in Figure 6.2.11 increasing the sediment velocities had as similar effect to increasing the diffusion in the pore water. The base values used in the model were based on typical settling velocities for sand, silt and biotic particles.

The calibration of the KETOX model is described in further detail in Section 4.1.3 of this report. The K-E submodel of KETOX was used to generate the local lateral eddy viscosity which is converted to a dispersion coefficient by a calibration factor that is assigned for each reach. The best results were obtained with a factor of 0.6 near the Dow outfalls, i.e. from the Cole drain to Suncor for a streamtube of about 40m from the Canadian shoreline. Outside of this zone and upstream of Stag Island the factor was 0.8. Downstream of Stag Island the best factor was 1.0. Figure 6.2.12 shows the agreement between the calibrated model and measurements made by MOE (Section 4.2.2) and CCIW (Chan et al. 1986). Figure 6.2.13 shows a verification plot of HCB along the Canadian shoreline for the reach from Cole drain to Suncor using 1986 investigative data and mean loads based on the long-term effluent monitoring (Section 4.1.1).

Under steady state conditions the main loss of contaminant from the aquatic system is through volatilization. The parameters that affect volatilization are: Henry's constant, the water and air currents, the water depth, water and air temperatures, molecular weight of the chemical, dissolved fraction in the water and the ambient air concentration. Since no reliable information is available on the air

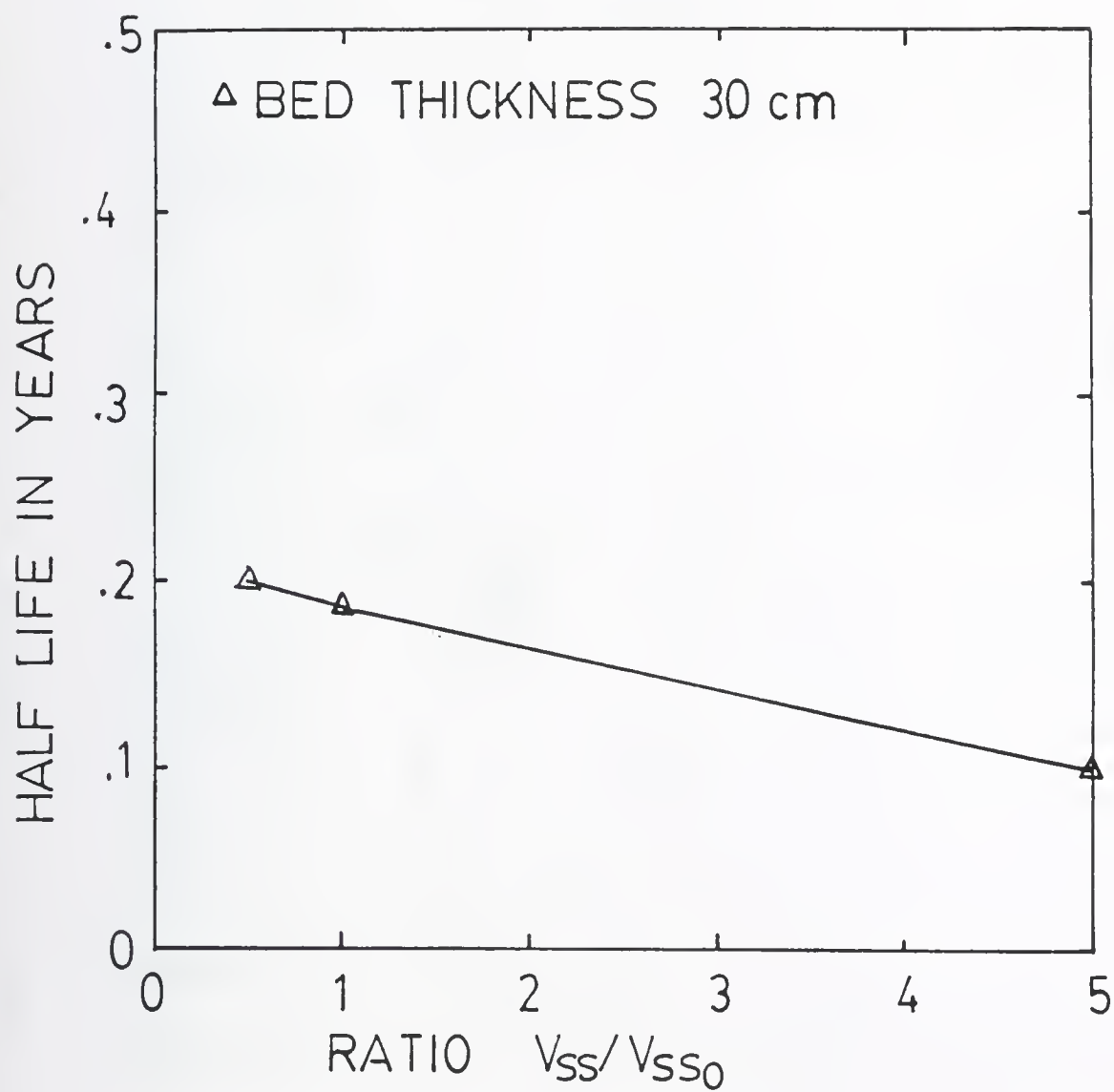


FIGURE 6.2.11: The Effect of Settling velocity on the Response Time of the Bed

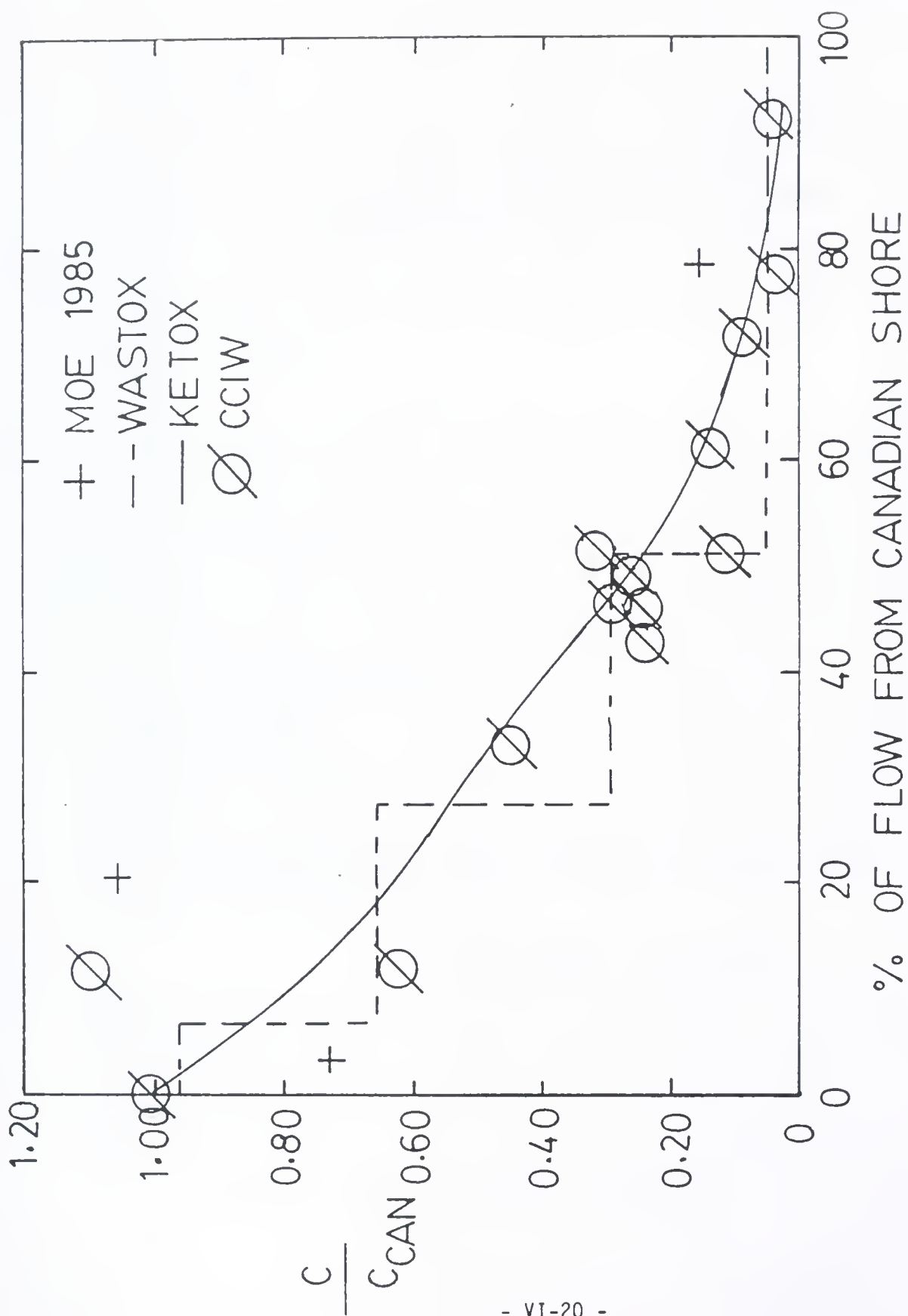
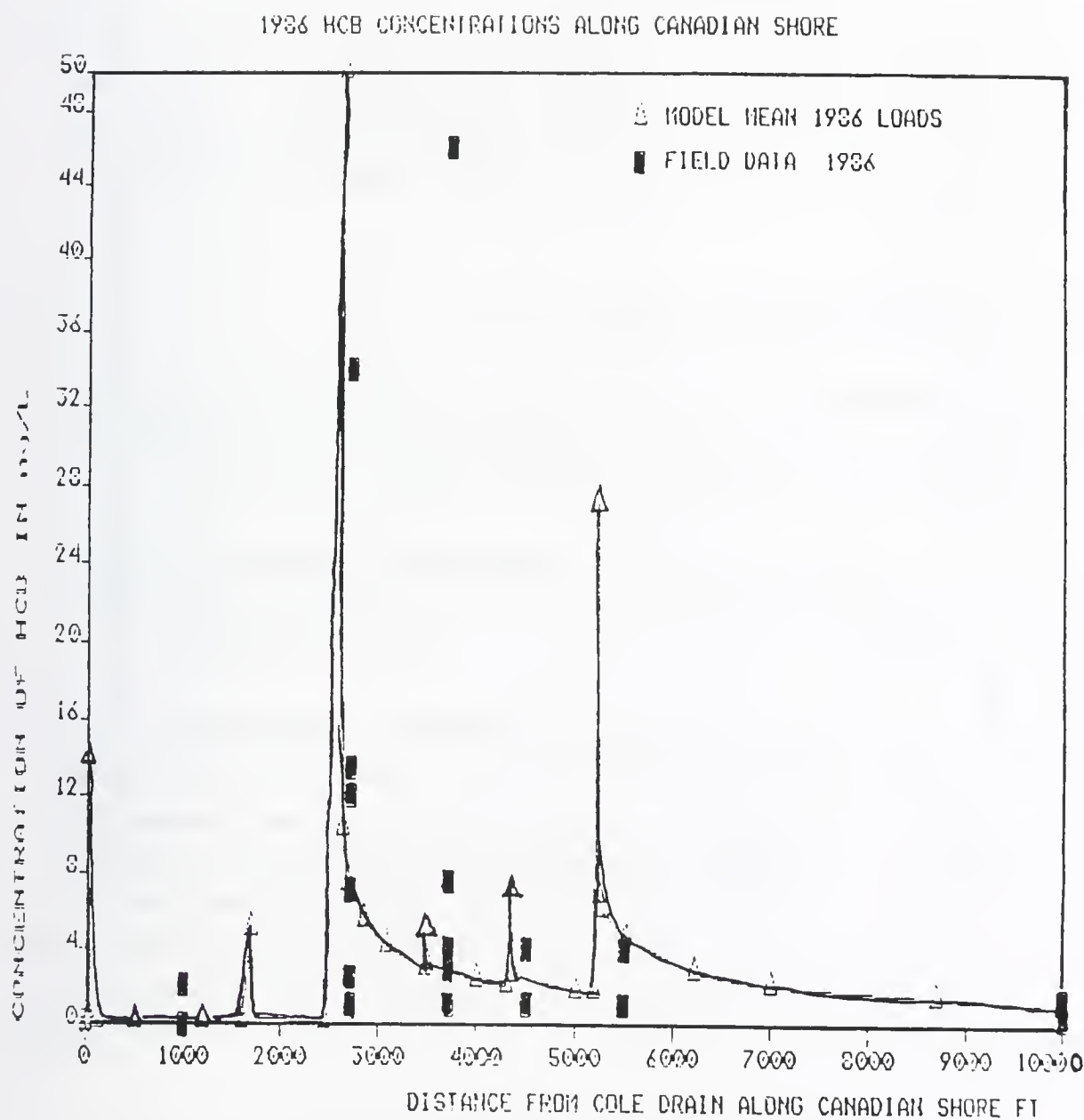


FIGURE 6.2.12: Comparison of the Predicted Concentration Profile with measured Data at Port Lambton



**FIGURE 6.2.13: Comparison of the 1986 Predicted and Investigative HCB Concentrations along the Canadian Shoreline in the vicinity of Dow Chemical**

concentrations these were assumed to be negligible. PERC and HCB were selected to illustrate the effect of various parameters on river concentrations. The reach from the Cole drain to Suncor was selected for a comparative analysis. Figure 6.2.14 summarizes the main results. The change in Henry's constant of 3 fold between HCB and PERC did not result in a significant increase in the loss of chemical for water depths of the order of 20 feet; similarly the loss was not significantly increased by doubling the air velocity. The loss was significantly increased at a river depth of 10 feet. Doubling of the water velocity also yielded a significant increase in the loss of chemical.

(b) The WASTOX Exposure and Foodchain Model

WASTOX (Water Quality Analysis Simulation for Toxics) which was developed by Dr. J.P. Connolly of Manhattan College, New York, consists of two independent submodels:

- 1) the exposure concentration submodel which simulates the transport, transfer, and reaction of toxic chemicals in water bodies;
- 2) the food chain submodel which determines the effects of toxic pollutants on individual species and communities of organisms.

WASTOX is a three dimensional unsteady transport model. The cell structure, as shown in Figure 6.2.15, is similar to WASP and TOXIWASP. Figures 4.1.25 through 4.1.28 define the cells used in the fine and coarse grid models of the St. Clair River. The main mechanisms which determine the fate of the pollutant in a water system are:

- (a) **transport**, the physical movement of the chemical caused by the advective movement of water, mixing, scouring, and deposition of solids;

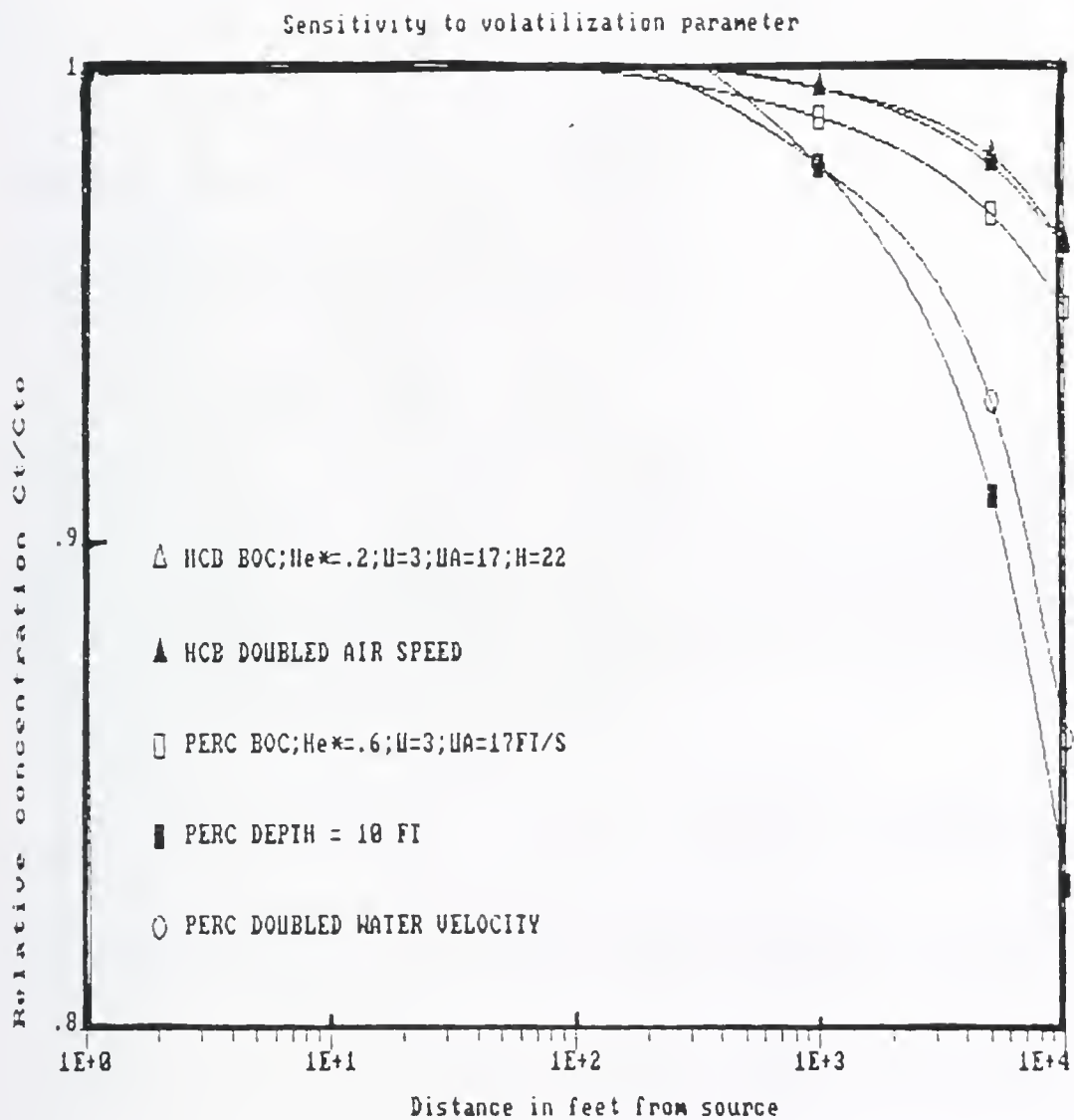
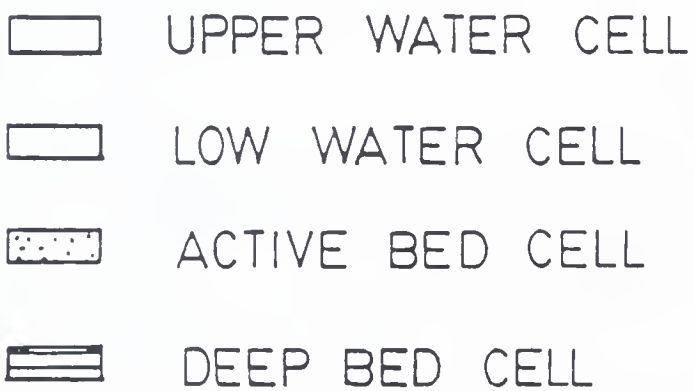


FIGURE 6.2.14: Sensitivity of contaminant Loss to Volatilization Parameters



- VI-24 -



- (b) **transfer**, the movement of the chemical between the air, water and solid phases. It includes volatilization and adsorption;
- (c) **reaction**, the transformation of the chemical. It includes biodegradation, photolysis, hydrolysis and oxidation.

The main assumptions of the model are that:

- (a) all segments are well mixed;
- (b) sorption is an instantaneous process within each segment;
- (c) the degradation processes are assumed to be first order.

The WASTOX model includes a generalized food chain which permits:

- (1) various predator-prey relationships,
- (2) age differentiation within species,
- (3) migration of species,
- (4) biological activity including respiration, growth, assimilation and bioaccumulation,
- (5) benthic and pelagic species.

Based on discussions subsequent to the MOE aquatic foodchain modelling workshop (MOE 1988b) a preliminary foodchain system was developed as shown in Figure 6.2.16.

Chemical and physical properties of the selected contaminants utilized by the model are presented in Table 4.1.9.

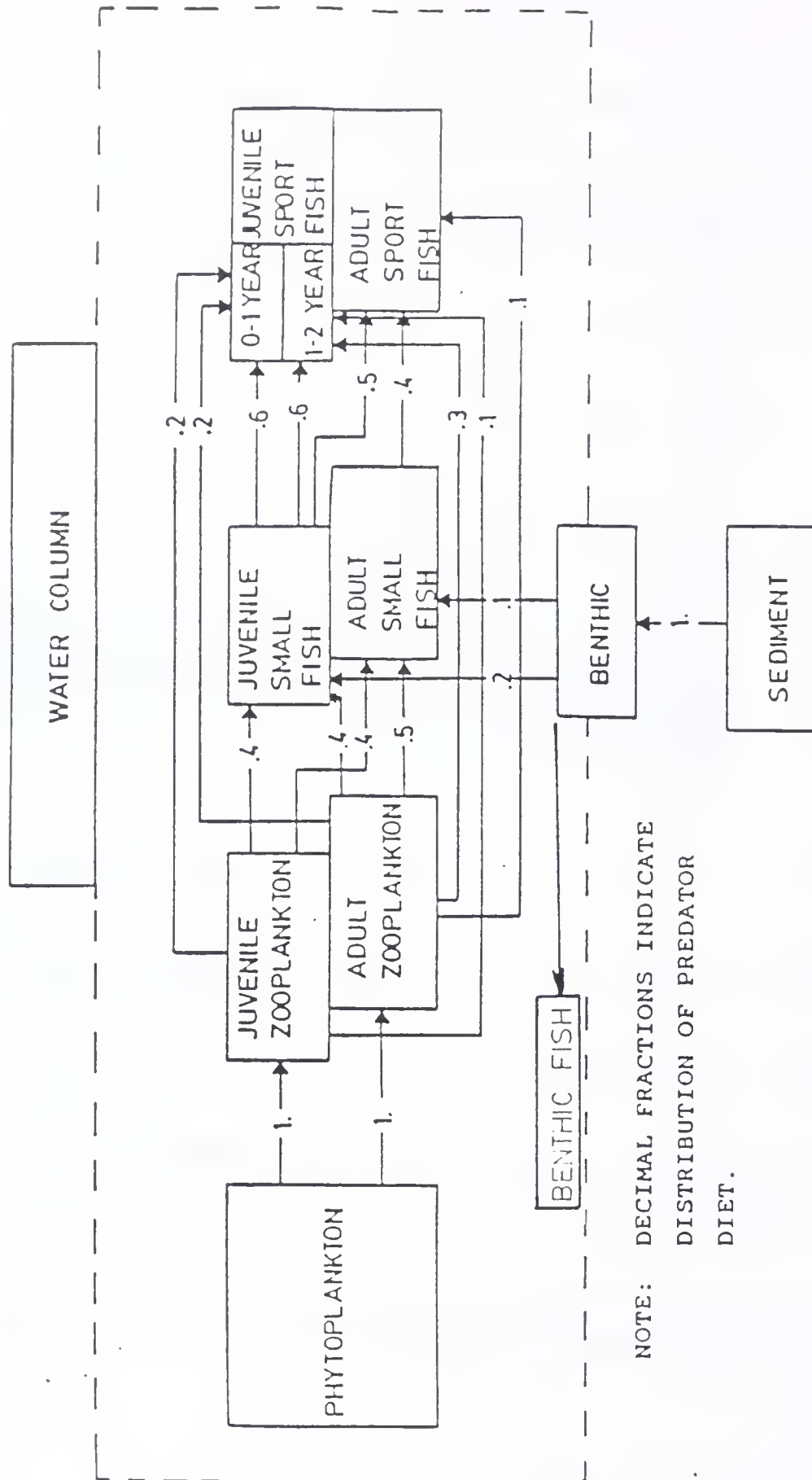


FIGURE 6.2.16: Preliminary Food Chain for Lake St. Clair/  
St. Clair River

The suspended sediment concentrations and suspended sediment loads were estimated based on the MISA Pilot Study data as well as data collected for the 1985 joint Federal-Provincial study of the St. Clair River (DOE/MOE 1986). The WASTOX model included three sediment sizes representative of fine (clay and/or biotic material), medium (silt), and coarse (sand and gravel). The MISA data set included information on the suspended sediment size distribution in the river and outfalls; however the analysis was limited to two size classes since sand and gravel were not normally in suspension (Sections 4.1.2 and 4.2.1).

Similarly the bed layer was assumed to consist of three sizes of sediment. The 1986 DOE/MOE report and the data from the MISA sediment survey were used to establish the river bed composition, which varied from hard clay to gravel. The active bed layer was observed to vary from less than a centimeter to more than 30 cm. In the middle part of the river there was very little granular bed material while near the shore there were sand and gravel deposits with thicknesses up to about 30 cm. The dunes and/or ripples on the sand and gravel deposits varied in height from a few cm to the full depth of the deposit. It was assumed the active bed depth in the sand and gravel areas was of the same order as the dune height. For modelling purposes the active bed depth was set at 15 cm at the shore and decreased to 3 cm at approximately 100m from shore.

The estimation of settling rates and resuspension fluxes were part of the initial calibration procedure. The starting values were obtained from the TOXIWASP model (McCorquodale et al. 1985) that had previously been developed for the Upper Great Lakes Connecting Channel study (UGLCCS 1989); however, since TOXIWASP uses only one sediment size, published data on settling velocities for clay, silt and sand were used to estimate the individual settling velocities in such a way that the weighted mean for the three sizes was similar to the value from TOXIWASP.

Since the steady state KETOX model is developed on the same fundamentals as the unsteady WASTOX and since the KETOX model gives much faster turn-around times (a few minutes on an AT microcomputer) than the WASTOX model (a few hours on the mainframe IBM 4381), the detailed sensitivity analyses and the initial calibration were made using KETOX. The velocity data were then transferred from the KETOX model to the WASTOX model. The initial values of the lateral diffusion coefficients in the WASTOX model were obtained from the K-E model. These coefficients were adjusted in the calibration process. The calibration process was carried out in stages: a) the sequential data was used to calibrate the fine grid WASTOX model for the reach from the Cole drain to Stag Island (Section 4.1.3). An overall calibration of the lateral dispersion coefficient was made for the entire river from the Cole drain to Port Lambton using 1985 data from MOE as well as published data from CCIW (Chan et al. 1986). The 1986-87 MISA long-term effluent loading and investigative field data were used for verification purposes.

Figure 6.2.12 shows the measured and predicted concentration profiles near Port Lambton.

The long execution times for WASTOX made it difficult to carry out extensive sensitivity analyses. It is noted that the time response of the bed as predicted by WASTOX for the fine grid (Cole drain to Stag Island) was of the order of 1/2 year while the overall response time for the entire river was of the order of 1 year; this is in reasonable agreement with the KETOX response times.

The food chain component of the WASTOX model was implemented on an AT microcomputer. HCB and OCS were selected as the contaminants for the model development. Tables 6.2.2 and 6.2.3 show the parameters that were used for HCB and OCS respectively.

TABLE 6.2.2: Parameter values for HCB food chain simulation

Species	G d <sup>-1</sup>	W0 gw	R d <sup>-1</sup>	β	γ	ρ o <sub>c</sub> <sup>-1</sup>	ν s/cm	ω	δ	φ o <sub>c</sub> <sup>-1</sup>	Lipid content %	BCF BCF μ/gw	Food assim. effic.	Toxicant assim. effic.	Fraction dry weight
Phytoplankton	-----	-----	-----	BETA	GAMMA	RHO	-----	OMGA	DLTA	PHI	-----	-----	-----	-----	-----
Benthic Invertebrate	.0089	.00007	.00144	.0157	.25	0.	0.	-----	-----	0.	1.	3.16	.3	.05	.2
0-8 mo.	.0143	.00021	-----	.0157	.25	0.	0.	0.	0.	0.	1.	3.16	.8	.15	.25
8-16 mo.	.0035	.0081	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
0-3 years	.00245	2.5	-----	.047	.2	0.	0.	0.	0.	0.	1.	3.16	.8	.35	.25
4-6 years	.00047	36.85	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
0-1 yr.	.0058	2.2	-----	.03	.295	0.	.022	2.79	.1285	0.	1.	3.16	.8	.6	.25
1-2 yrs.	.0058	18.3	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Adult Sport Fish 2-12 years	.0003	153.6	-----	.03	.295	0.	.022	2.79	.1285	0.	1.	3.16	.8	.7	.25

log K<sub>ow</sub> = 5.5  
Diffusivity = 7.03 x 10<sup>-6</sup> cm<sup>2</sup>/s

TABLE 6.2.3: Parameter values for OCS food chain simulation

Species	G d <sup>-1</sup>	W0 gw	R d <sup>-1</sup>	B	γ	ρ o <sub>C</sub> <sup>-1</sup>	ν s/cm	ω	δ	φ o <sub>C</sub> <sup>-1</sup>	Lipid content %	BCF BCF μ/gw	Food assim. effic.	Toxicant assim. effic.	Fraction dry weight
Phytoplankton	-----	-----	-----	BETA	GAMMA	RHO	-----	OMGA	DLTA	PHI	1.	15.8	-----	-----	.1
Benthic Invertebrate	.0089	.00007	.00144	.0157	.25	0.	0.	-----	-----	0.	1.	15.8	.3	.35	.2
Zooplank- ton	.0143	.00021	-----	.0157	.25	0.	0.	0.	0.	0.	1.	15.8	.8	.35	.25
Small Fish 0-3 years	.00245	2.5	-----	.047	.2	0.	0.	0.	0.	0.	1.	15.8	.8	.4	.25
Adult 4-6 years	.00047	36.85	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	.5	-----
Juvenile Fish 0-1 yr.	.0058	2.2	-----	.03	.295	0.	.022	2.79	.1285	0.	1.	15.8	.8	.6	.25
1-2 yrs.	.0058	18.3	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Adult Sport Fish 2-12 years	.0003	153.6	-----	.03	.295	0.	.022	2.79	.1285	0.	1.	15.8	.8	.6	.25

log K<sub>OW</sub> = 6.2  
Diffusivity = 6.08 × 10<sup>-6</sup> cm<sup>2</sup>/s

Figure 6.2.17 shows the simulated body burden for HCB in adult sport fish in Mitchell's Bay for 1985 along with the 1985 MOE field data. The predicted seasonal and age variations are also indicated in Figure 6.2.17. Figure 6.2.18 shows the corresponding predicted and field data for OCS. Figures 6.2.19 and 6.2.20 show the predicted body burdens in the Delta St. Clair River and in selected cells of Lake St. Clair for HCB and OCS based on 1985 loads and bed conditions. Figure 6.2.21 shows the predicted variation of body burden with trophic level for HCB and OCS; this illustrates that bioaccumulation (uptake from water and food) is higher for OCS ( $\log K_{OW} = 6.2$ ) than for HCB ( $\log K_{OW} = 5.5$ ) which agrees with the findings of Thomann (1988) and Gobas and Mackay (1988).

(c) The TOXIWASP Exposure model

The TOXIWASP model was selected for Lake St. Clair because it incorporated the advantages of WASP (DiToro et al. 1981) and EXAMS (Burns et al. 1982) and adds the sediment water interaction. Moreover it was proven to be useful for toxic chemicals in a Great Lakes environment (Great Lakes Institute 1986). In addition, the TOXIWASP model was used to check the validity of the results of the WASTOX model.

TOXIWASP includes the main transfer mechanisms to account for the interactions between the dissolved chemical both with suspended solids and with stationary sediments in the riverbed. These mechanisms include:

- (1) advection and dispersion of dissolved contaminants;
- (2) settling contributions from point/non-point sources of solids and contaminants into the water;
- (3) volatilization and biological degradation.



LAKE St. Clair - WASTOX - HCB  
HCB Concentration in ADULT SPORT FISH

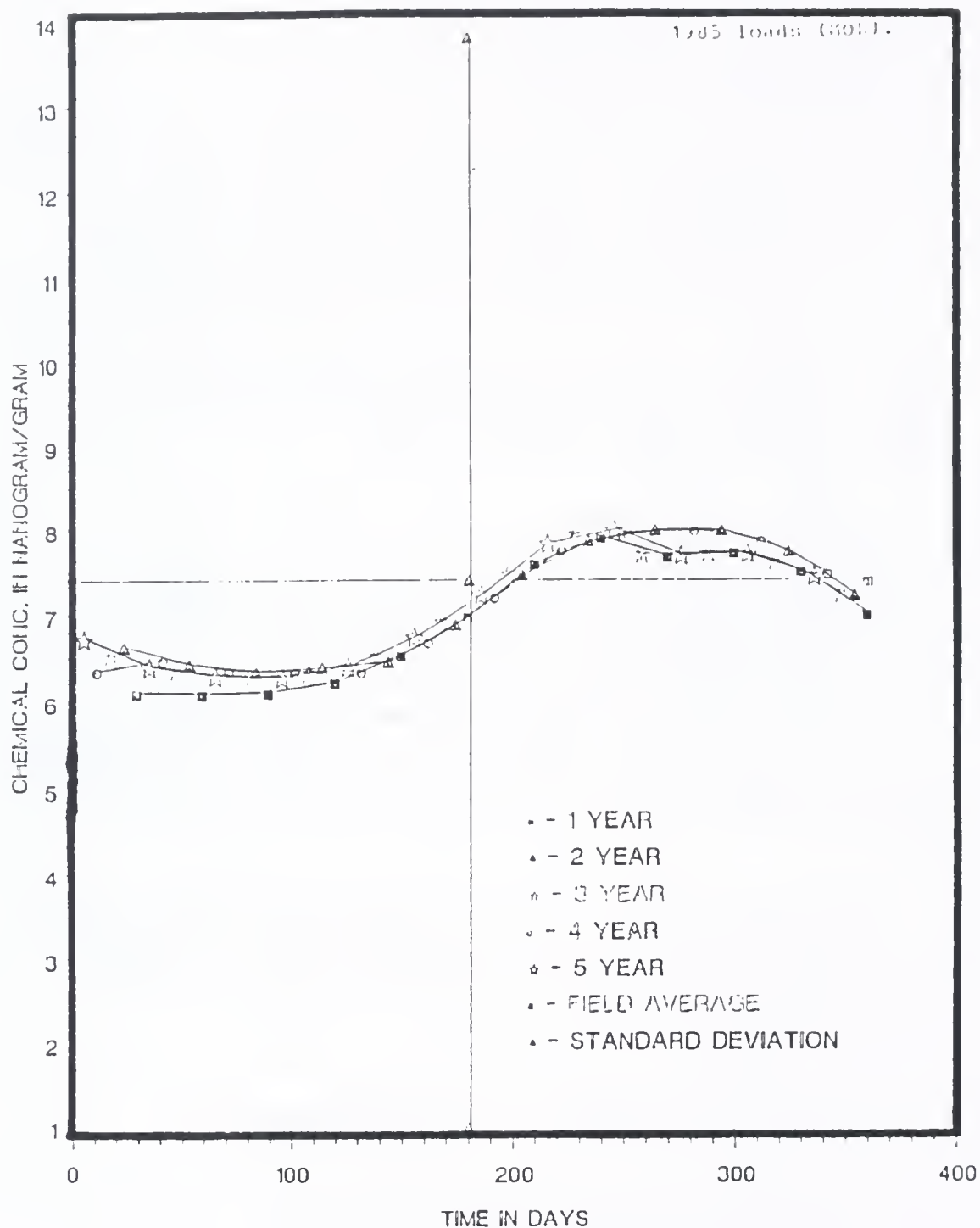


FIGURE 6.2.17: Predicted and Measured HCB Body Burdens in Adult Sport Fish in Mitchell's Bay (1985)

LAKE St. Clair - WASTOX - OCS  
OCS Concentration in ADULT SPORT FISH

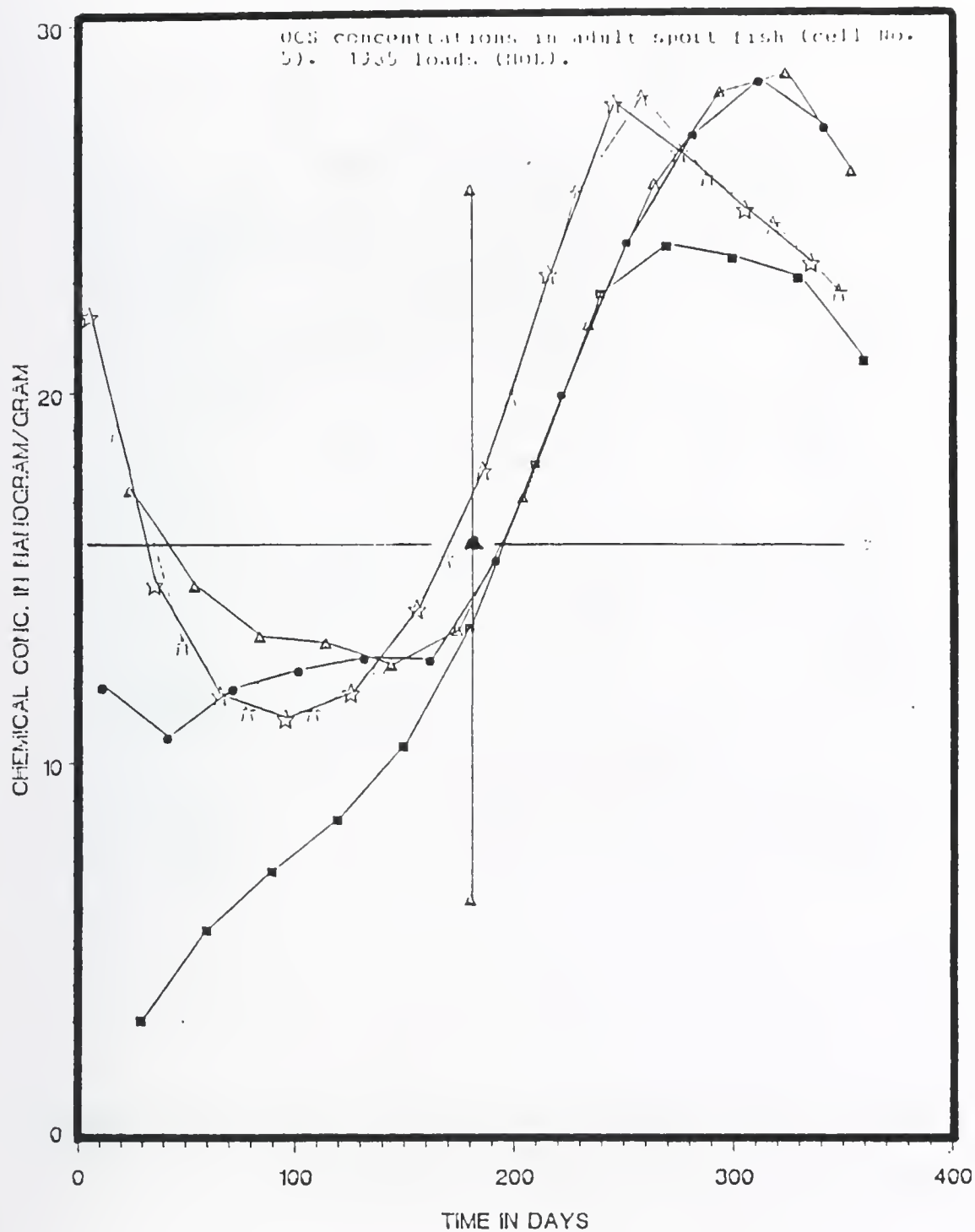
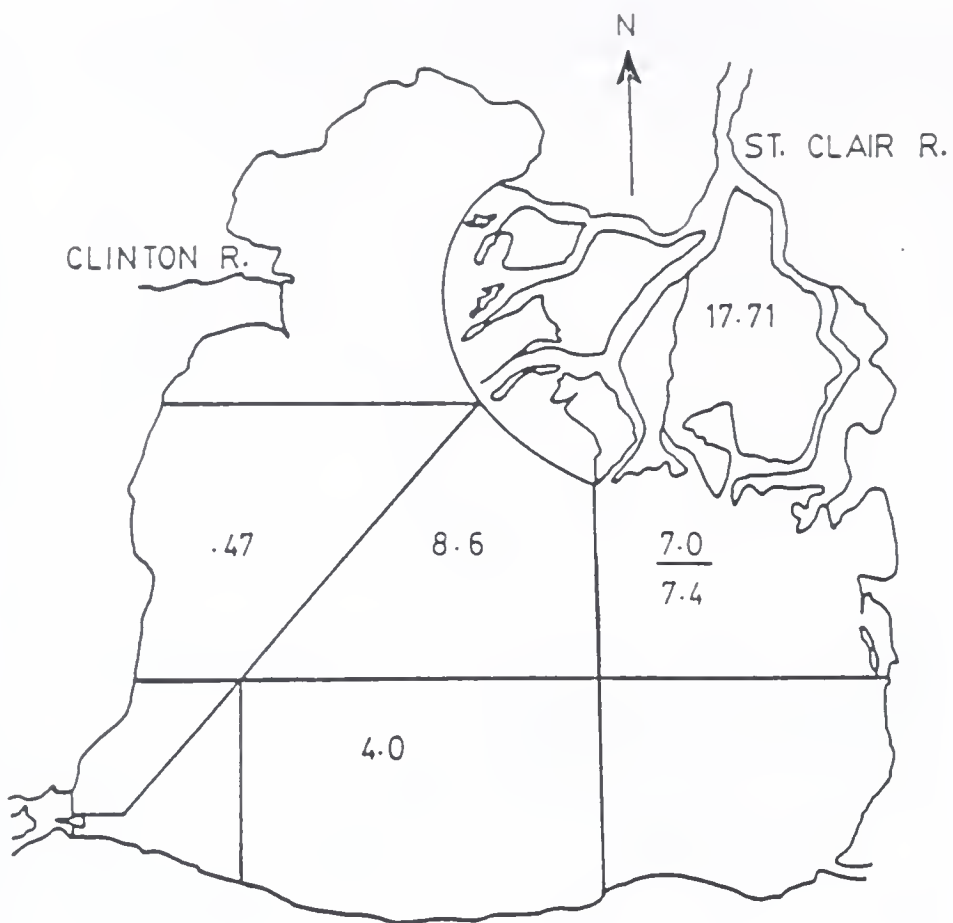


FIGURE 6.2.18: Predicted and Measured OCS Body Burden in Adult Sport Fish in Mitchell's Bay (1985)



$\frac{\text{WASTOX}}{\text{MOE}}$  (ng/g wet wt)

FIGURE 6.2.19: Predicted Distribution of HCB in Adult Sport Fish in Lake St. Clair

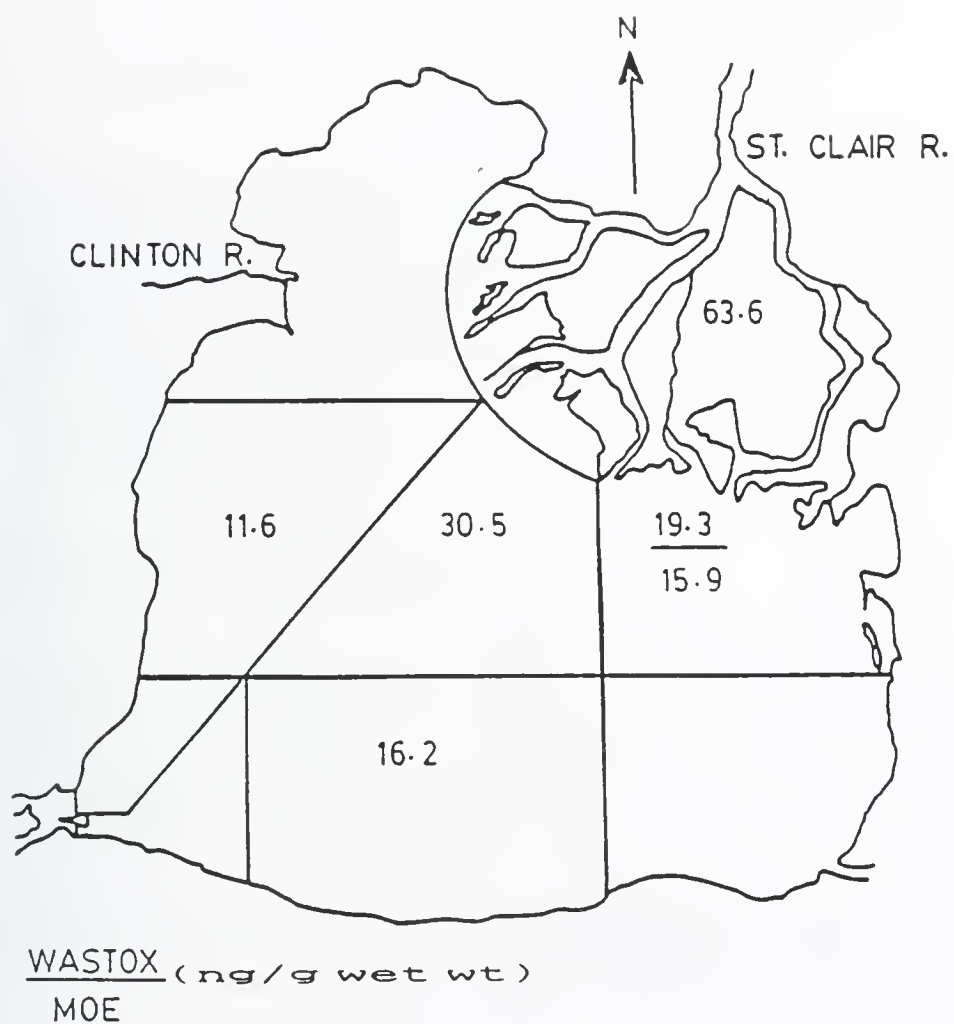
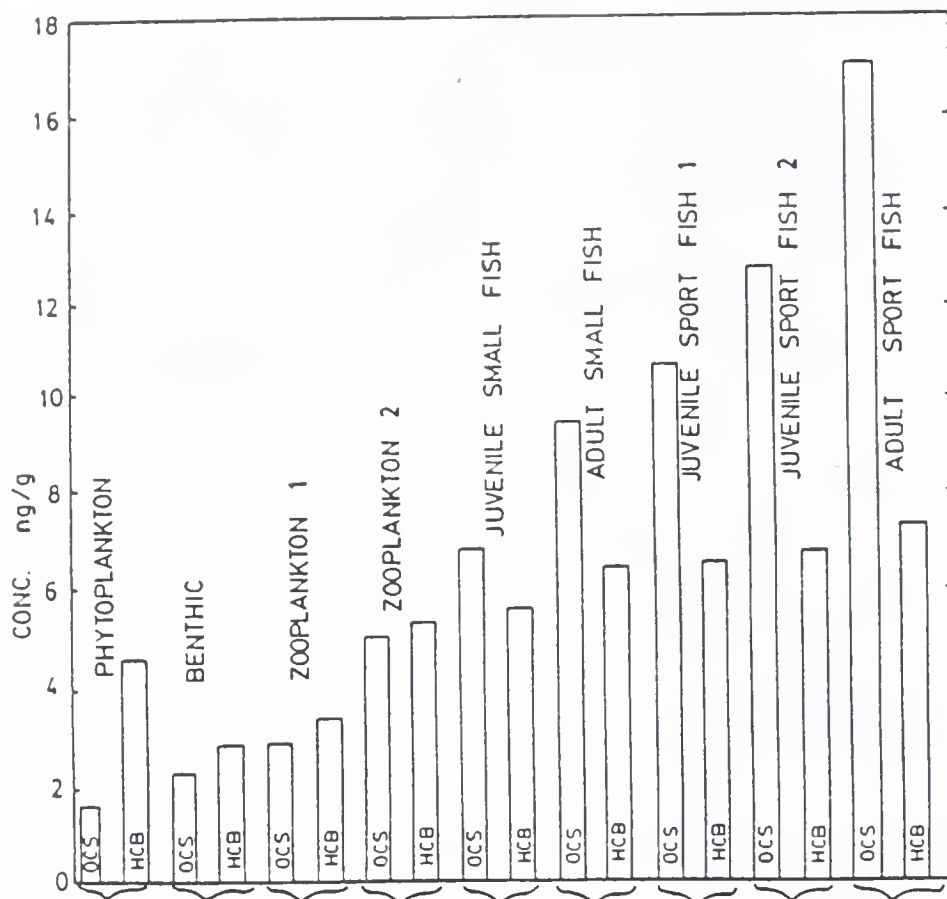


FIGURE 6.2.20: Predicted Distribution of OCS in Adult Sport Fish in Lake St. Clair



**FIGURE 6.2.21: Body Burden of HCB and OCS in the Species of the WASTOX food Chain for Lake St. Clair (1985)**

Volatilization is a major mechanism by which many dissolved contaminants leave the water column. The TOXIWASP model treats volatilization by the two film concept that is used by its predecessor, EXAMS (Burns et al. 1982).

The TOXIWASP model that was used for Lake St. Clair was originally developed by Ibrahim (1986). This model was calibrated using PCB and OCS data. It was estimated that the response time for the lake is of the order of 3 years. Figures 6.2.22 and 6.2.23 shows the computed distribution of HCB and OCS in the waters of Lake St. Clair based on 1985 loads.

(d) The Thomann Generic Food Chain Model

At the Ministry of the Environment Aquatic Food Chain Modelling Workshop held in July 1987 at Seneca College, Dr. R.V. Thomann of Manhattan College proposed a four trophic level generic food chain model (MOE 1988b). The steady state version of Dr. Thomann's model was used in this study. The trophic levels were distinguished by mass as illustrated in Figure 6.2.24. Phase partitioning was assumed for the first level (phytoplankton) while subsequent levels were assumed to obtain contaminants from both water and food. It was further assumed that a particular trophic level feeds only on the level immediately below it. The variables included in the model are:  $K_{ow}$ , lipid fraction at each trophic level, mass of organism at each trophic level, food assimilation efficiency, contaminant assimilation efficiency, growth and respiration constants, and dissolved concentrations in the water. The uptake rate is a function of the efficiency of transfer as given by Thomann and Mueller (1987) and Thomann (1987). The output of the model is the concentration in the lipid and whole body of the organism.

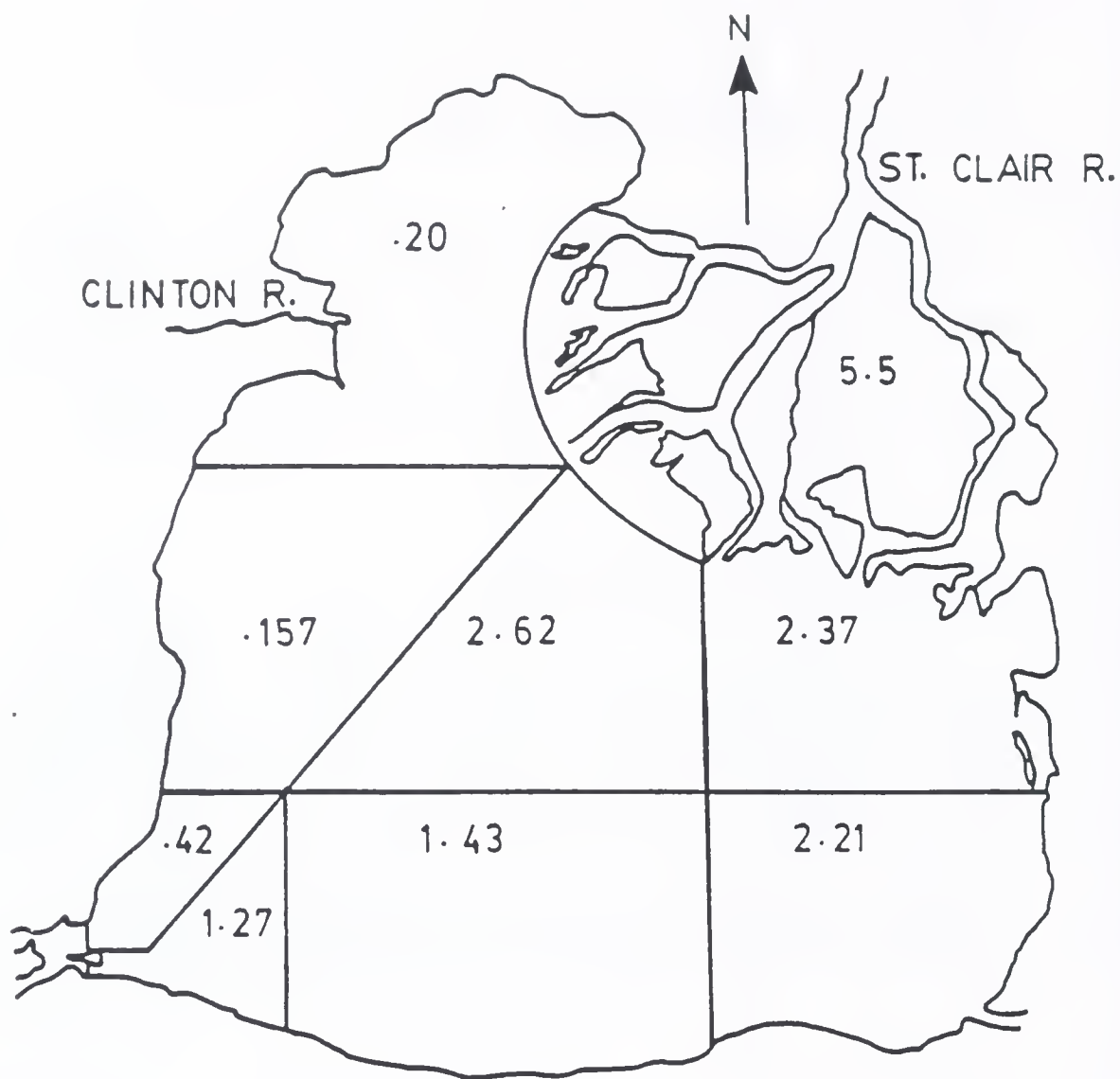


FIGURE 6.2.22: Predicted Total HCB Concentrations in Water Cells of Lake St. Clair in ng/L for 1985



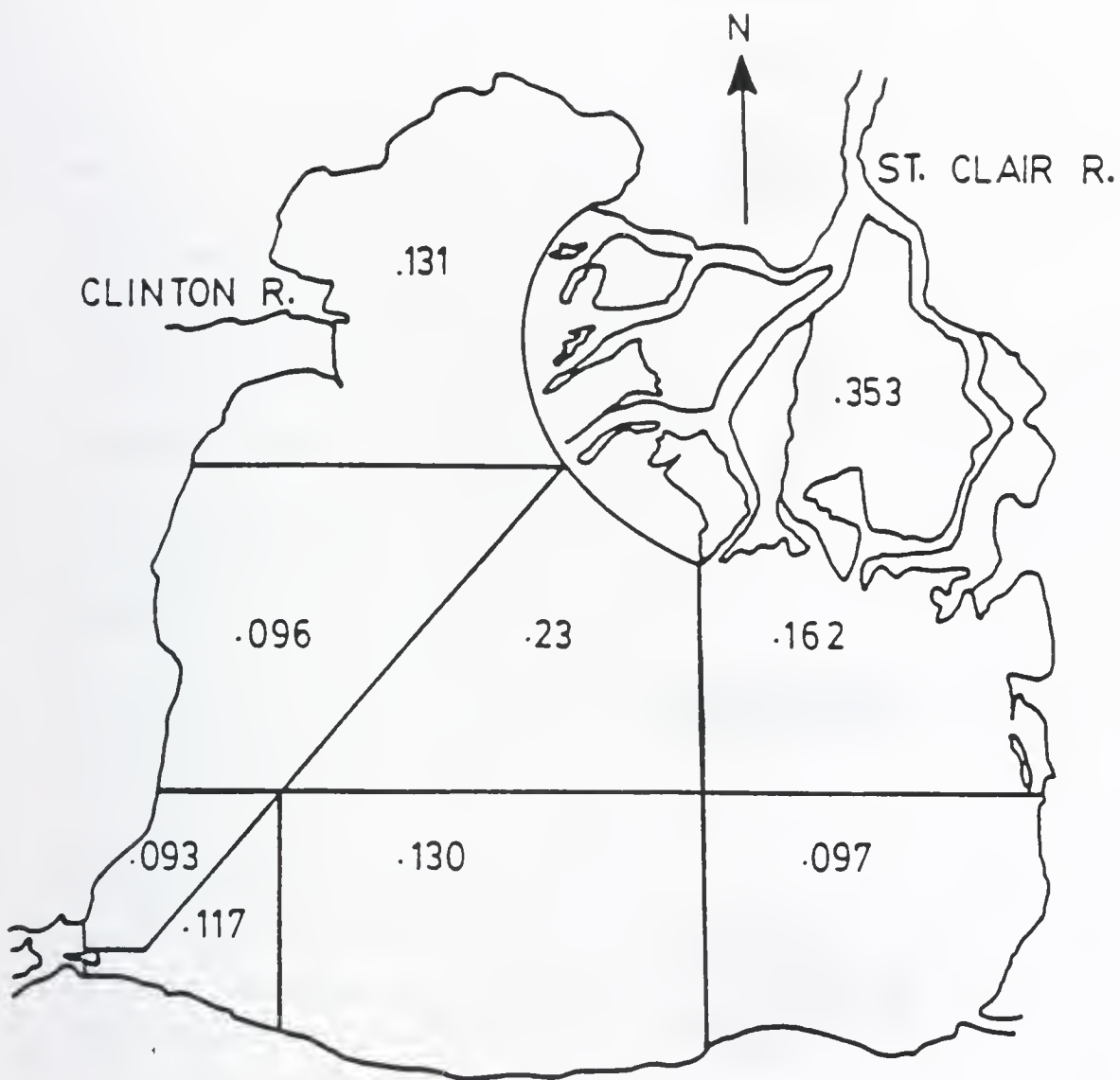
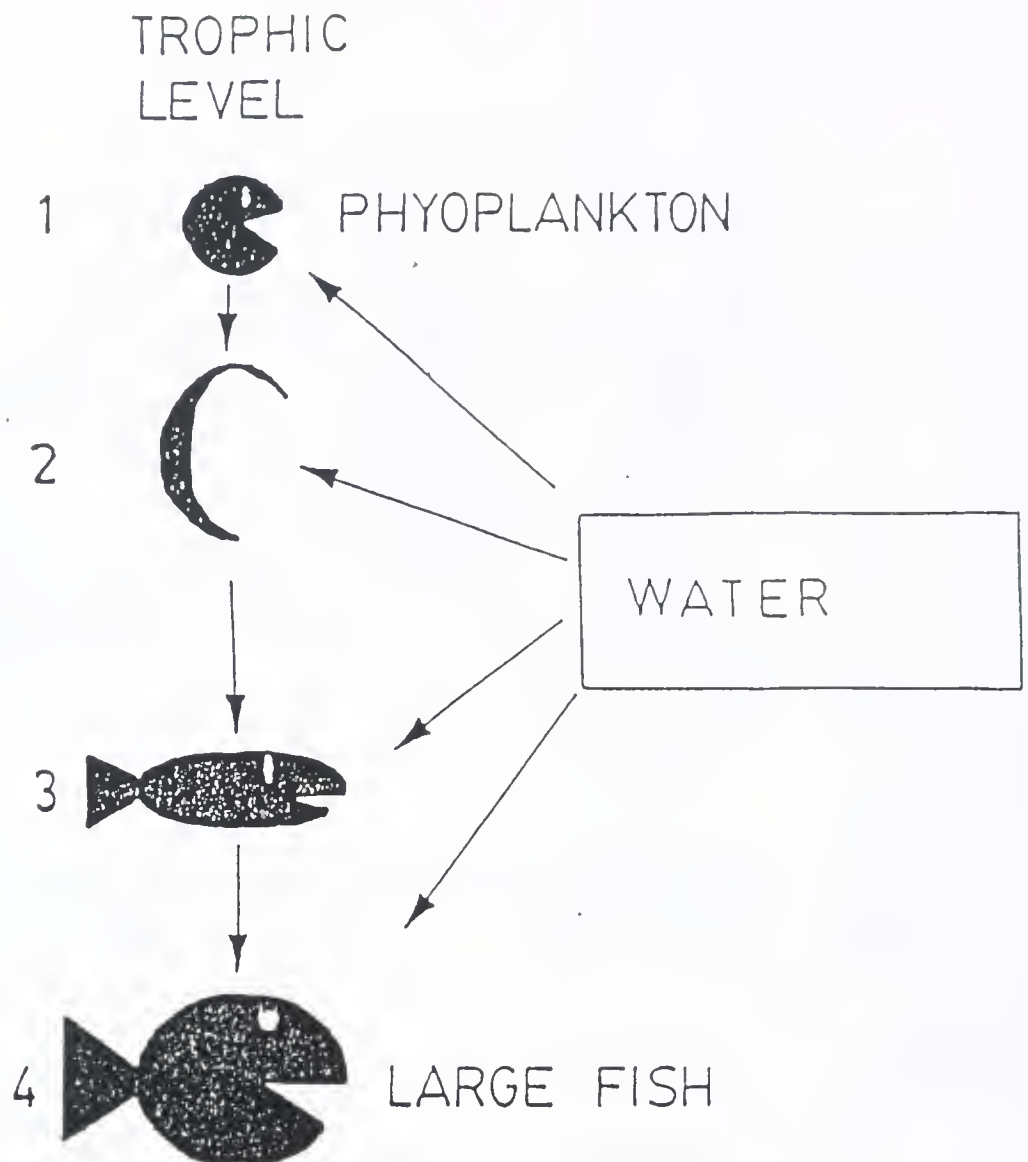


FIGURE 6.2.23: Predicted Total OCS Concentrations in Water Cells of Lake St. Clair in ng/L for 1985



*FIGURE 6.2.24: Simplified 4 Level Generic Food Chain  
[After Thomann (1987)]*

(i) Sensitivity Analysis - Thomann Generic Food Chain Model

A sensitivity analysis was performed on this model in conjunction with the KETOX exposure model. The response of various trophic levels in the food chain to modifications in control parameters was examined. The following parameters were varied: food assimilation, respiration rate, growth rate, suspended solids in the water column, chemical  $K_{ow}$  and partition coefficient for suspended solids. The food chain body burden response to contaminant concentrations in the water column is linear and is dealt with in the section on load allocation. Table 6.2.4 summarizes the responses of the highest trophic level in the model (sportfish) to changes in model parameters. The body burden was found to be highly sensitive to lipid fraction, food assimilation efficiency and respiration rate. The model output was much less sensitive to growth related parameters. In all cases the sensitivity was greater for OCS than for HCB. Body burdens increased with increasing lipid levels, increasing respiration rates and decreasing food assimilation efficiency.

Figure 6.2.6 indicates the dissolved fraction of a contaminant depends on the partition coefficient and the concentration of suspended solids. Since the direct uptake from the water is assumed to be from the dissolved phase (bioavailable phase) an analysis was made to determine the food chain response to the combined effects of suspended solids,  $K_{ow}$  and fraction TOC (fc). The results are shown in Figure 6.2.25. Figure 6.2.25 is for sportfish and is based on a unit total exposure concentration e.g., 1 ng/L. The most significant effect of suspended solids is for chemicals with log  $K_{ow}$  greater than 6 where the maximum effect can be a four fold decrease in body burden.

TABLE 6.2.4: SENSITIVITY ANALYSIS FOR SPORTFISH MODEL  
PARAMETERS

Chemical	LOG K <sub>ow</sub>	C <sub>w</sub>	C <sub>x2</sub> / C					
		ng/L	[C in sport fish for doubled parameter]/ [ Reference C]					
			Lipid Food Asim a	beta β	gamma γ	delta δ	phi φ	
HCB	5.5	1.2	3.6* 0.5**	0.99*	1.1*	1.1*	1.8*	
OCS	6.2	0.16	5.5* .15**	1.3*	0.7*	0.7*	4.5*	

Rates: Respiration =  $R = \phi / W^\gamma = \delta / W^\delta$   
 Growth =  $G = \delta / W^\beta = \delta / W^\beta$   
 Consumption =  $C = (G+R)/a$

\* Reference parameters: lipid=.025;a=0.8;beta=0.2;gamma=0.2;  
delta=.01;phi=.036.

\*\*Reference parameters: lipid=.025;a=0.4;beta=0.2;gamma=0.2;  
delta=.01;phi=.036.

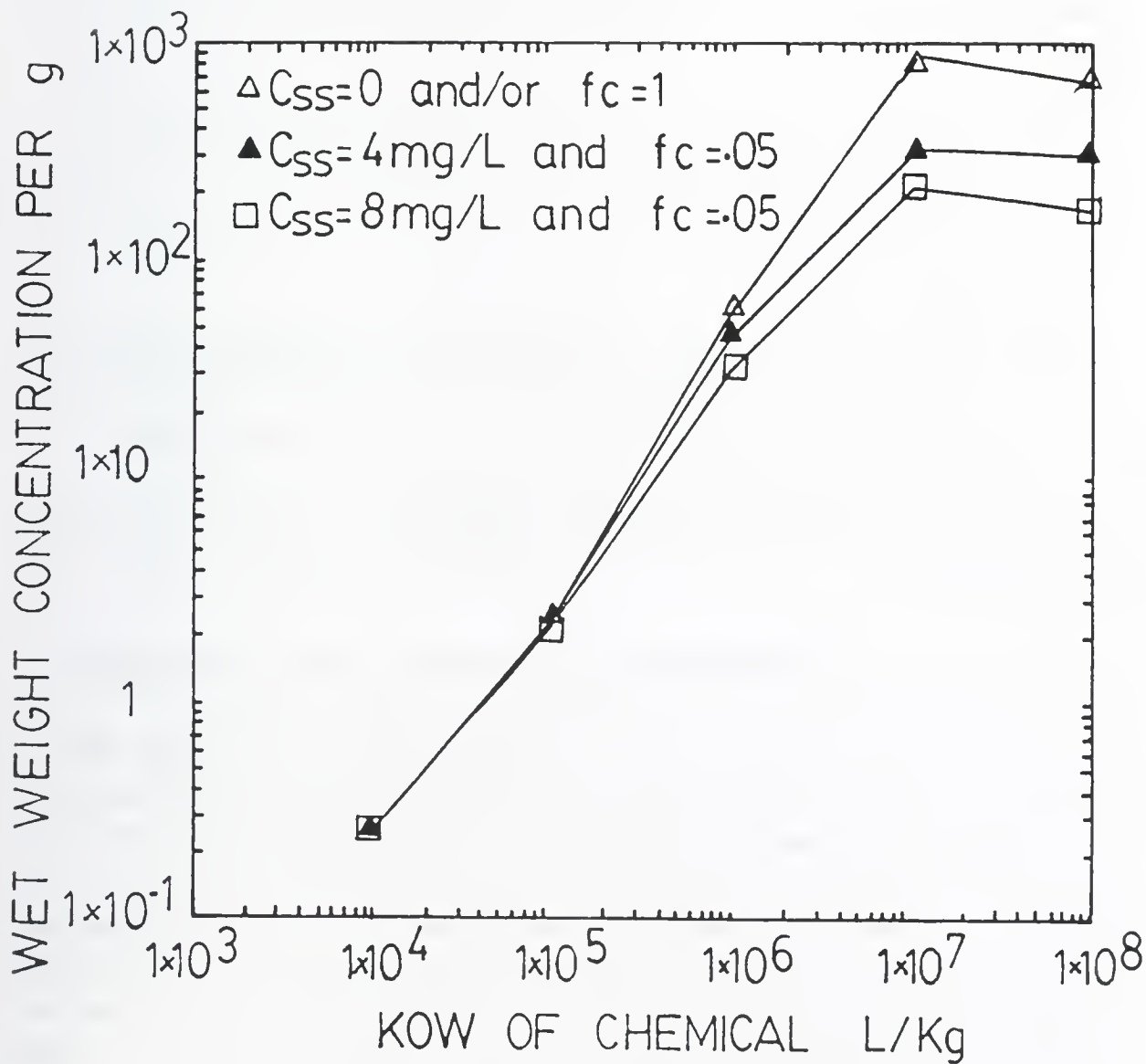


FIGURE 6.2.25: Effects of Kow, TOC and Suspended Solids on Body Burden in Fish

### 6.3 Mixing Zone Definition

In a river such as the St. Clair which has multiple outfalls and intakes, the plume from one outfall may significantly interfere with that of other outfalls. Ultimately if there were enough dischargers, the river could be impaired along its entire length which would have an adverse effect on aquatic biota in the river. In order to protect all users and to comply with MOE Policy related to mixing zones ("Blue Book" - Policy 5), it is suggested that the following guidelines be used in assigning a length of a mixing zone (MZ):

- (a) MZs should not be continuous. In order to avoid this it is suggested that MOE policy guidelines should be met at or before the nearest downstream user, including intakes and/or outfalls of the same owner;
- (b) when the alternative users are the biota, allowance must be made for the right-of-passage outside of the MZ as well as reasonable access to acceptable shoreline habitats and resting areas.

These guidelines conform to the existing MOE Policy 5 guidelines for mixing zones (MOE 1984).

Since fish tend to be attracted to the warm plumes of the outfalls it is important that the concentrations in the initial mixing zone are not acutely toxic at any point. Large scale model studies (Abdel-Gawad 1985) suggest that vertical uniformity of concentration is achieved in 4 to 10 local depths (depending on the densimetric Froude Number which is the ratio of inertial to gravity forces) downstream of the shore based outfall. Therefore, if the MZ is limited to 4 to 10 times the local river depth, a vertical contaminant gradient will exist, ensuring that a less contaminated layer through which fish can pass will be present. Normally the plume is buoyant and the benthic organisms are subject to lower water concentration than those measured at the surfaces; however, as the plume attaches to the bed, the exposure of benthic organisms increases.

Thus, for the typical slightly buoyant plume it is expected that the bed concentrations may reach a maximum between 4 and 10 local depths downstream of the outfall if  $D_{jet} < H/4$  as shown in Figure 6.3.1 where  $D_{jet}$  is the effective diameter of the effluent and  $H$  is the river depth.

For the purposes of conducting waste load allocations, the following options with respect to delimiting the MZ were considered, with the most restrictive being utilized:

(1)  $X_C < \Delta X$

(2)  $Y_C < W/4$

where  $W$  is the local river width,

(3)  $X_C < C_m H$

(4) in no case is the present load permitted to increase nor is the existing MZ allowed to get larger.

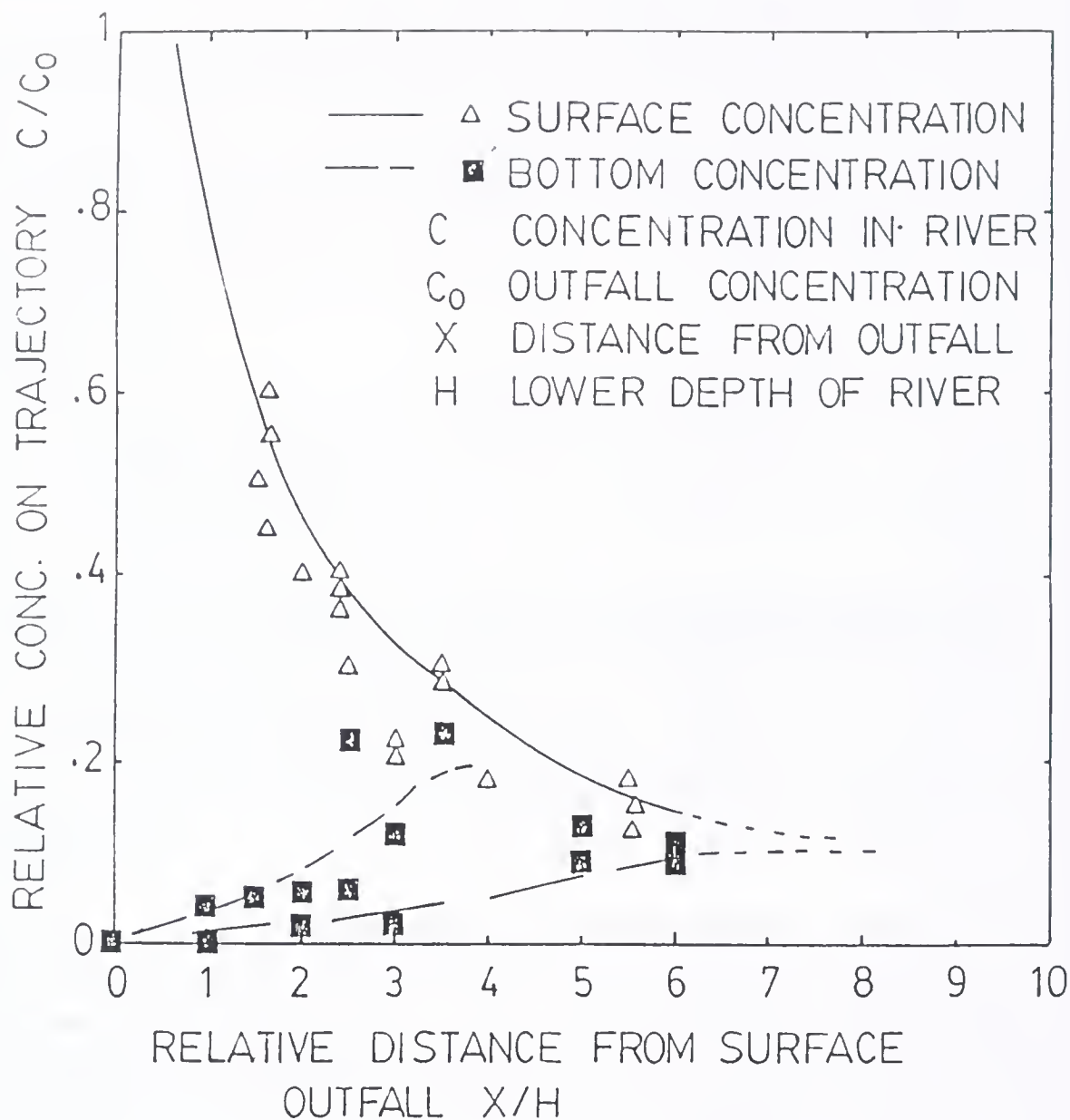
$\Delta X$  is the distance in the direction of flow to the next outfall or intake;  $H$  is the average local river depth in the MZ;

$D_{jet}$  is the effective diameter of the effluent;  $X_C$  = length of MZ and  $Y_C$  = width of MZ.

#### 6.4 Environmental Quality Criteria Considered for Use

The water quality criteria for whole water, (Table 6.4.1) sediment and biota (Table 6.4.2) were compiled for selected contaminants from several agencies including the Ontario Ministry of the Environment, the Canadian Council of Resource and Environment Ministers (CCREM), U.S. EPA, the Michigan Department of Natural Resources and the New York State of Department Environmental Conservation. In the absence of a MOE or other agency water quality criteria, a conservative advisory was developed. This value is based on limited toxicological information, and as such has a high margin of safety. Once further information is made available, it is likely





**FIGURE 6.3.1: Variation of the Surface and Bottom Concentrations at Slightly Buoyant Shore Based Outfalls**  
 [After Abdel-Gawad (1986)]

that these advisories will become less restrictive. Preliminary guidelines/advisories for other parameters of concern and/or for the protection of sensitive users are also given in Table 6.4.2.

## 6.5 Statistical Considerations in Developing Load Allocations

The two computer models give an estimate of the local depth averaged concentration. These predictions are directly related to the input loads assigned in the model and inversely related to the assigned river flows. The models have been calibrated based on measured loads and the associated concentrations and river flow. A calibration error has been estimated for the model as the root mean square difference between the predicted and measured concentrations. Near the outfalls the sequential data was used to estimate this error. In the rest of the river investigative and historical data were used. A plot of this error relative to the local maximum concentration ( $S_m / C_{max}$ ) is plotted in Figure 6.5.1 as a function of distance from the dominant outfall. The Dow 1st St. 42-inch sewer was treated as the dominant outfall since for several contaminants the largest loads were from this source. It was not possible to isolate the effect of a single outfall, therefore the error shown to some extent represents the composite effect of all the outfalls. All field data have been corrected to depth averaged values and if necessary the model loads were computed based on integration of the flow and observed concentrations in the river. The sequential river concentrations for PERC and CCL4 indicated a higher mass loading than did the effluent measurement; in order to remove the loading related error between the model and the field ambient data, the loads were first modified to be consistent with the river measurements and then the model predictions were based on the modified loads. The same procedure was used in estimating the model error at Port Lambton. Thus the model calibration error is more or less independent of errors in the load estimate and independent of the variation in the river flow. The following relationship is proposed to account for the effects of river flow and load variability:

TABLE 6.4.1: SUGGESTED WATER QUALITY CRITERIA

SUBSTANCE	Water Quality Criteria (mg/L)	Source
Hexachlorobenzene	.0000065	PWQO <sup>1</sup>
Hexachlorobutadiene	.0001	CCREM <sup>2</sup>
Hexachloroethane	.013	Michigan <sup>3</sup>
Carbon Tetrachloride	.027	Michigan <sup>3</sup>
Tetrachloroethylene	.26	CCREM <sup>2</sup>
Octachlorostyrene	.0000001	MOE <sup>4</sup>
2,4,5 - Trichlorotoluene	.000107	MOE <sup>4</sup>
Mercury	.0002	PWQO <sup>1</sup>

LEGEND:

- <sup>1</sup> - MOE Provincial Water Quality Objective for the Protection of Aquatic Life.
- <sup>2</sup> - CCREM Water Quality Guideline for the Protection of Aquatic Life.
- <sup>3</sup> - Michigan Department of Natural Resources Guideline for the Protection of Aquatic Life.
- <sup>4</sup> - Ontario Ministry of the Environment tentative advisory: conservative value based on limited toxicological information. More information required to develop Provincial Water Quality Objective (PWQO) or Guideline (PWQG).

TABLE 6.4.2: EXISTING AND CALCULATED CRITERIA FOR BIOTA AND  
SEDIMENT

SUBSTANCE	Biota Criteria (µg/g)	Sediment Criteria (µg/g)
Hexachlorobenzene	.33 .0064 <sup>2</sup> .0017 <sup>3</sup> .00036 <sup>4</sup>	0.08 <sup>6</sup>
Hexachlorbutadiene	1.3 <sup>1</sup>	-
Hexachloroethane	14.1 <sup>1</sup>	-
Carbon tetrachloride	0.02 <sup>1</sup>	
Octachlorostyrene	0.02 <sup>1</sup>	-
Mercury	0.5 <sup>5</sup> 0.133 <sup>3</sup> 0.028 <sup>4</sup>	0.3 <sup>7</sup>

LEGEND FOR TABLE 6.4.2:

1. Non-carcinogenic fish flesh criteria to protect piscivorous wildlife as developed by New York State (NYS) Dept. of Env. Conservation (1987).
2. U.S. EPA draft fish consumption guideline for the protection of human health ( $10^{-6}$  Cancer risk) based on average U.S. fish consumption levels of 6.5 g/day.
3. Calculated value based on existing consumption guideline corrected for fish consumption by the average Ontario angler of 24.7 g/day.
4. Calculated value based on existing consumption guidelines corrected for fish consumption by an Ontario high fish consumer e.g., First Nation Walpole Island Indian Band (117 g/day).
5. Ontario Ministry of the Environment fish consumption guideline.
6. Draft bulk sediment guideline for the protection of benthic invertebrates as submitted to MOE through external contract. MOE has not yet endorsed the approach or guideline.
7. Ontario Ministry of the Environment dredging guideline.

$$C(x,y) = C_{mo}(x,y) \{L/L_{50}\} \{Q_{50}/Q\}$$

where  $C(x,y)$  = the actual concentration for a given load,  $L$  and river flow,  $Q$

$C_{mo}(x,y)$  = modelled concentration at the median monthly load,  $L_{50}$  and the median flow in the river  $Q_{50}$ .

It is assumed that the variances in  $C_{mo}$ , in  $Q$  and the load are random and independent; then an estimate of the variance or the square of the deviation from a median value in the local  $C(x,y)$  can be obtained by:

$$V_C = V_{sm} + V_Q + V_L$$

$V_C = S_C^2$  = the square error in  $C(x,y)$  or its transform

$V_{sm} = S_m^2$  = the square of the error in  $C_{mo}(x,y)$  or its transform

$V_Q = S_Q^2$  = the square of the deviation on  $Q$  or its transform

$V_L = S_L^2$  = the square of the deviation in  $L$  or its transform.

For illustrative purposes the deviations are taken as the differences between: the 5 % exceedence values and the median on the normalized cumulative frequency curves in the logarithm domain,  $C_{mo}$  and  $L$ ; and the 95% exceedence value and the median for  $Q$ . For each outfall and each contaminant the long-term effluent load measurements were averaged for the months of measurement; these data are referred to as the mean monthly loads. All of the subsequent analyses are based on these data sets. It is noted that the variability in the instantaneous data is considerably greater than for the mean monthly data. As an example for HCB at the Dow 1st Street 42-inch sewer the ratio of the instantaneous 5% exceedence load to the 50% exceedence load based on the sequential data was about 16 while

the mean monthly data gave a ratio of about 5 as indicated in Figure 6.5.2. The mean monthly frequency curves were selected because a one month period is more representative of the response of the aquatic ecosystem to changes in load. When acute toxicity is the critical factor, then the instantaneous frequency curves should be used; thus for acute toxicity within the MZ it is suggested that 5% exceedence loads be set at 3.2 times those obtained from the mean monthly data. Figures 6.5.3 to 6.5.7 show typical mean monthly normalized load frequency curves for HCB, HCB<sub>D</sub>, HCE, PERC and CCL<sub>4</sub> for two of the major point sources i.e. the Cole drain and the Dow 1st St. 42-inch sewer. The mean monthly data appear to fit a log-normal distribution. In Figure 4.1.36 it was shown that the instantaneous loads do not appear to fit the log-normal distribution when the extreme data are included.

The mean monthly river flow frequency curve is shown in Figure 6.5.8. A log normal curve was fitted to the mean monthly discharges for the St. Clair River. The actual discharges were estimated based on mean monthly stages and an approximate stage discharge curve. Also shown is the normalized flow frequency curve.

Figure 6.5.1 shows the estimated calibration error in KETOX and WASTOX with distance from the source. The error shown is the root mean square of the difference between the model prediction of concentration in the water column plotted against the distance as measured from the Dow 1st Street sewers complex. For several contaminants this represented the most significant point source along the shoreline. The Cole drain was also a significant source for several chemicals but because of the high dilution it did not give rise to large prediction errors. The errors have been normalized by dividing by the local maximum concentration predicted by the model, i.e. the maximum concentration in the cross-section where the measurement was taken. Figure 6.5.9 shows the error distribution curves corresponding to the calibration errors in Figure 6.5.1. A log normal distribution has been assumed for consistency with the load and flow distribution curves. Figure 6.5.9 was obtained by plotting on log normal paper, the ratio  $S_m/C_{max}$  and its reciprocal at the 16 and 84% exceedence levels respectively and then joining these two points with a straight line.



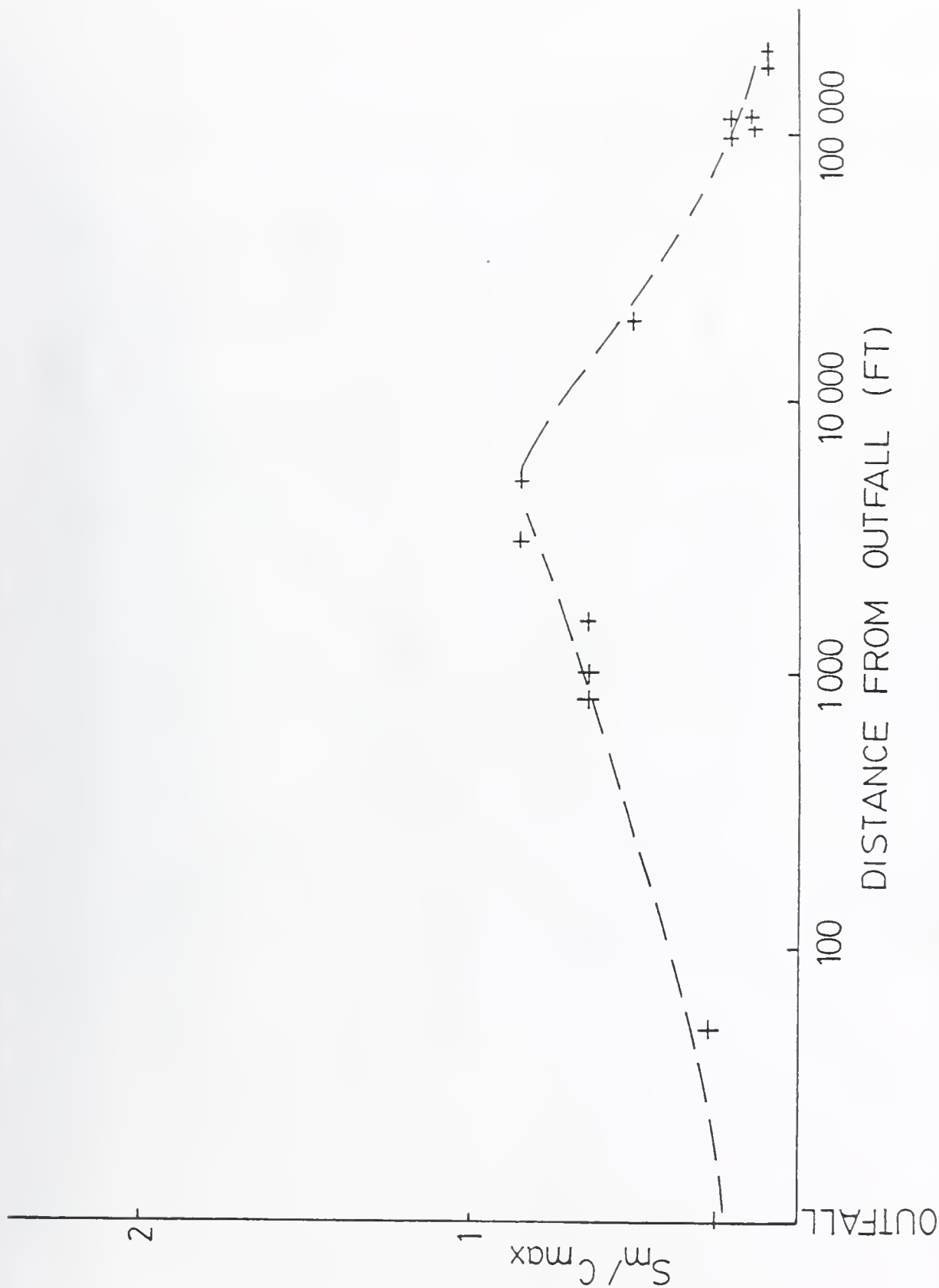


FIGURE 6.5.1: Model Calibration Error Versus Distance From the Load Source

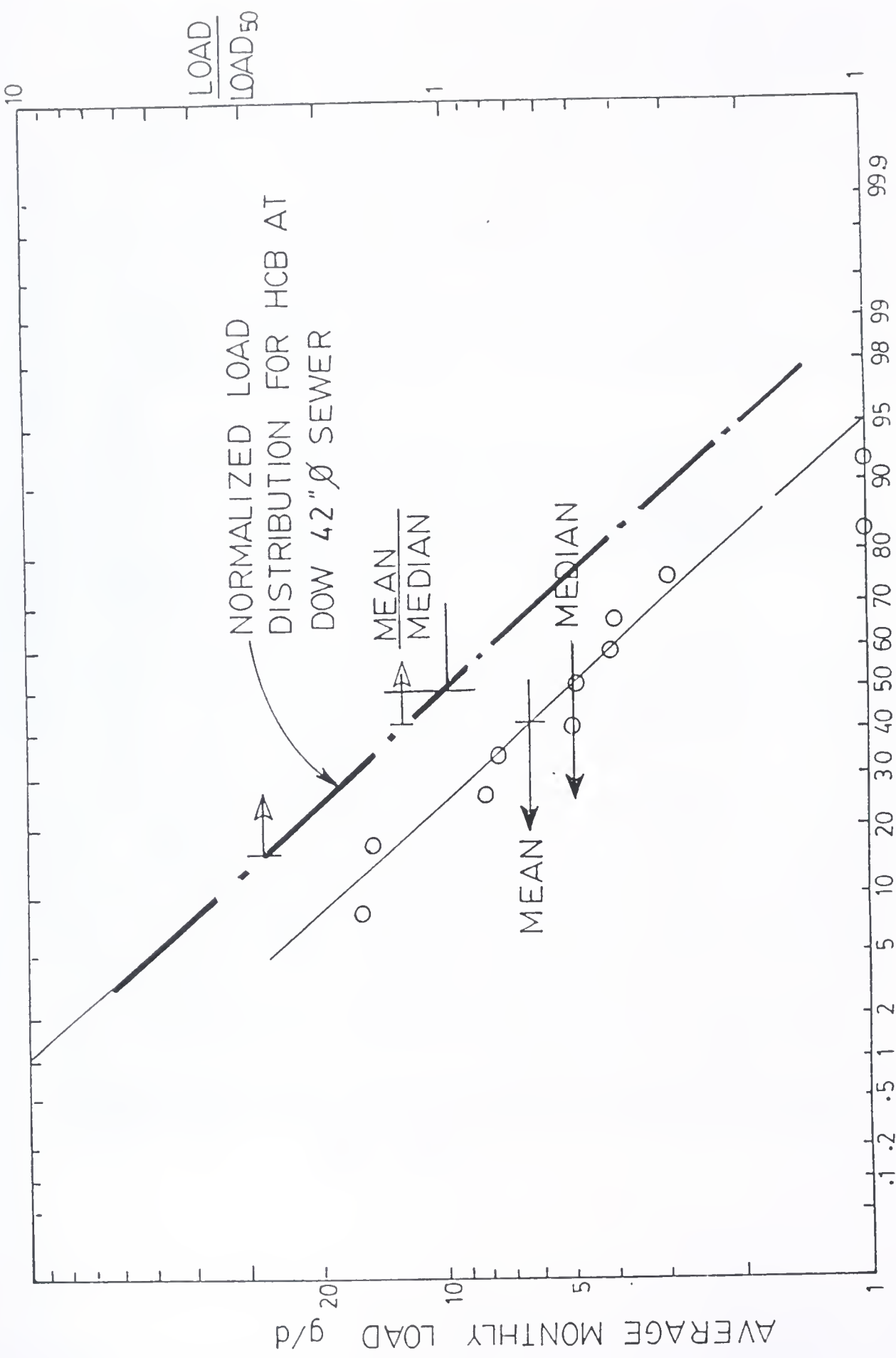


FIGURE 6.5.2: Load Frequency Curve for HCB at the Dow 1st Street sewer complex based on the 1986-1987 Mean Monthly Loads.

FIGURE 6.5.3: Normalized Load Frequency Curve for the  
Cole Drain for HCB, HCB D, HCE, PERC and CCL4

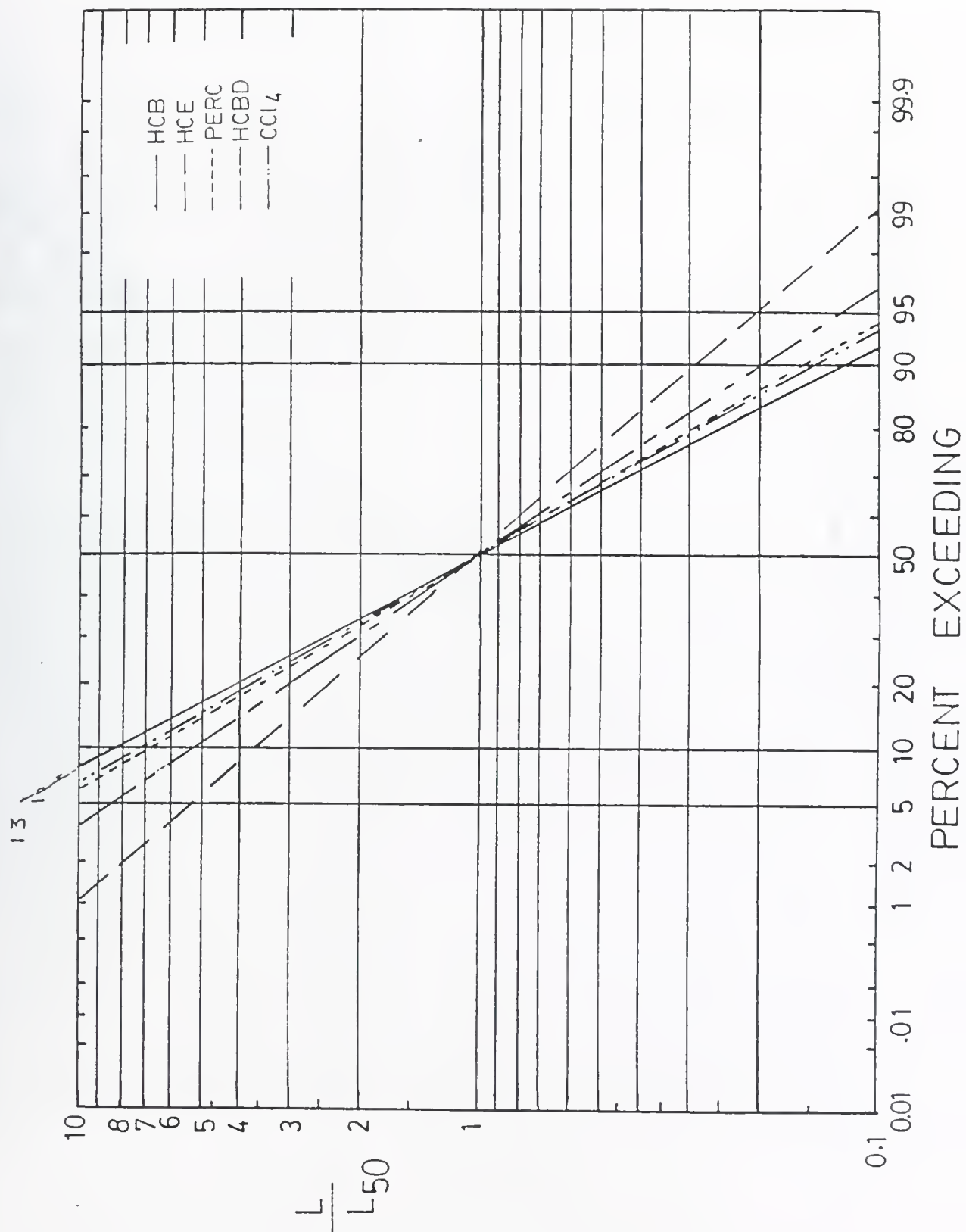


FIGURE 6.5.4: Normalized Load Frequency Curve for the  
Dow 1st street sewer complex for HCB, HCBBD,  
HCE, PERC and CCL4

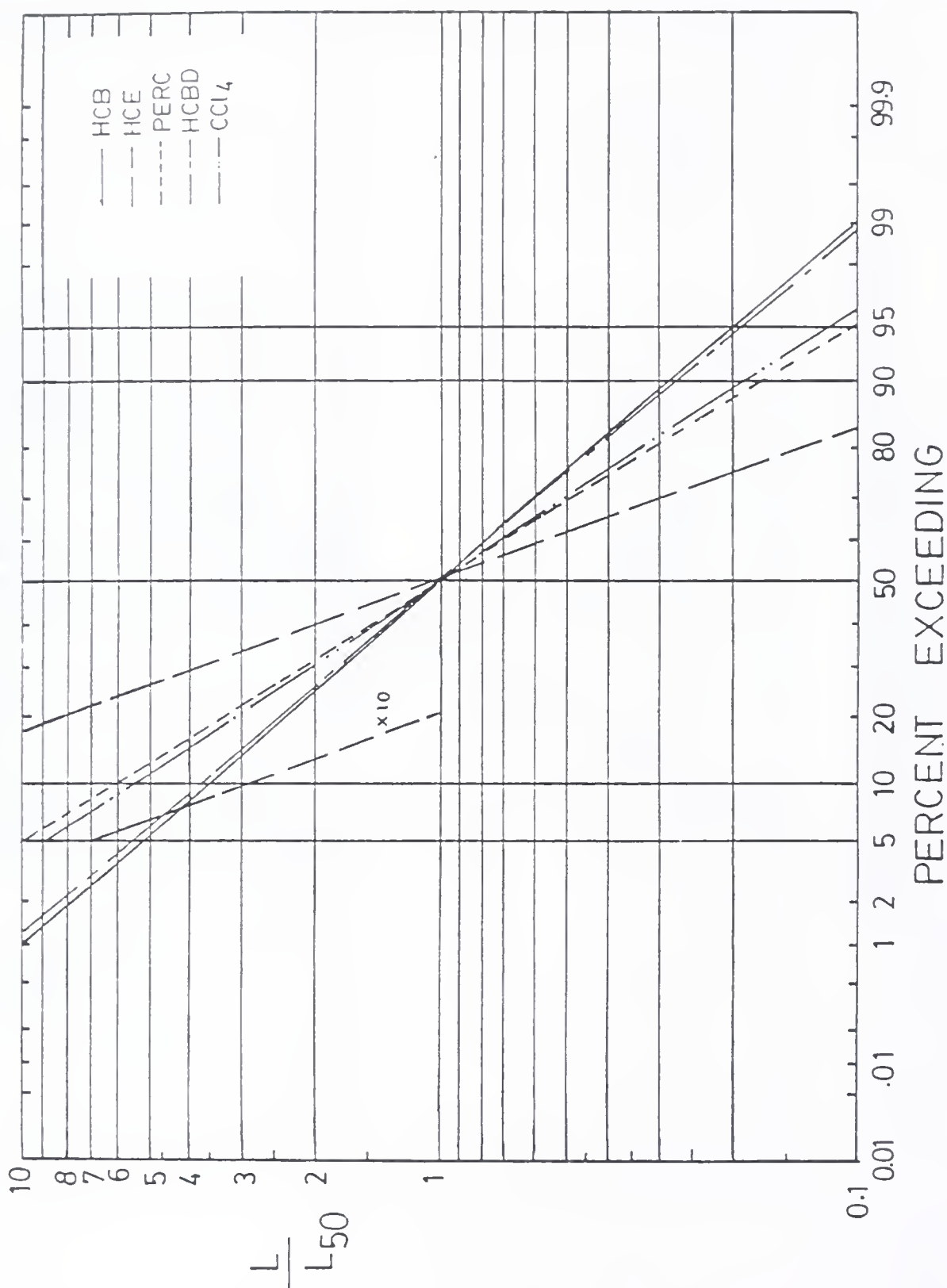


FIGURE 6.5.5: Normalized Load Frequency Curve for the Dow  
2nd Street sewer for HCB, HCE, PERC, HCB, HCE, PERC  
And CCL4

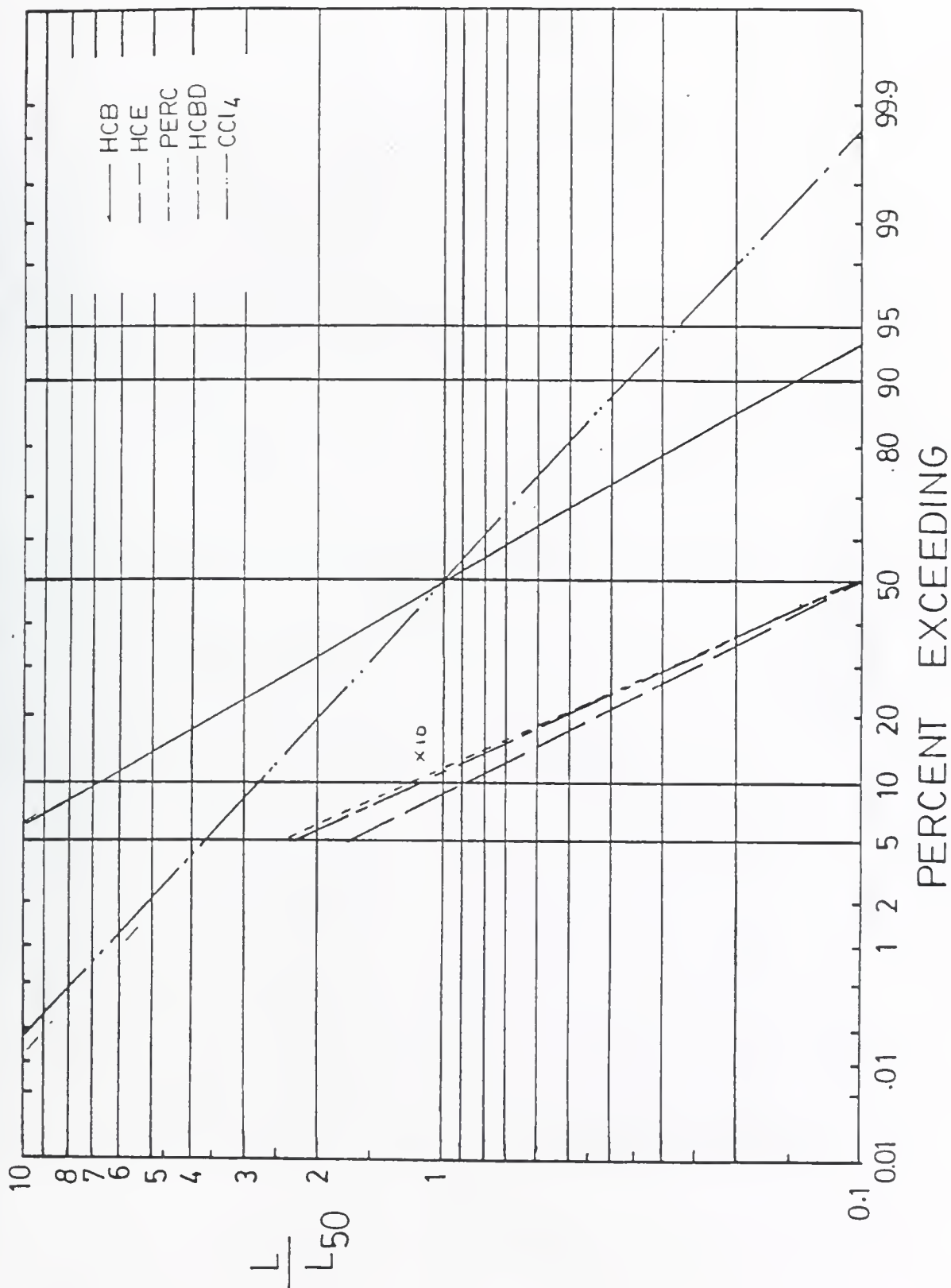


FIGURE 6.5.6: Normalized Load Frequency Curve for the Dow  
3rd street sewer for HCB, HCE, PERC, HCB, HCE, PERC  
CCL4

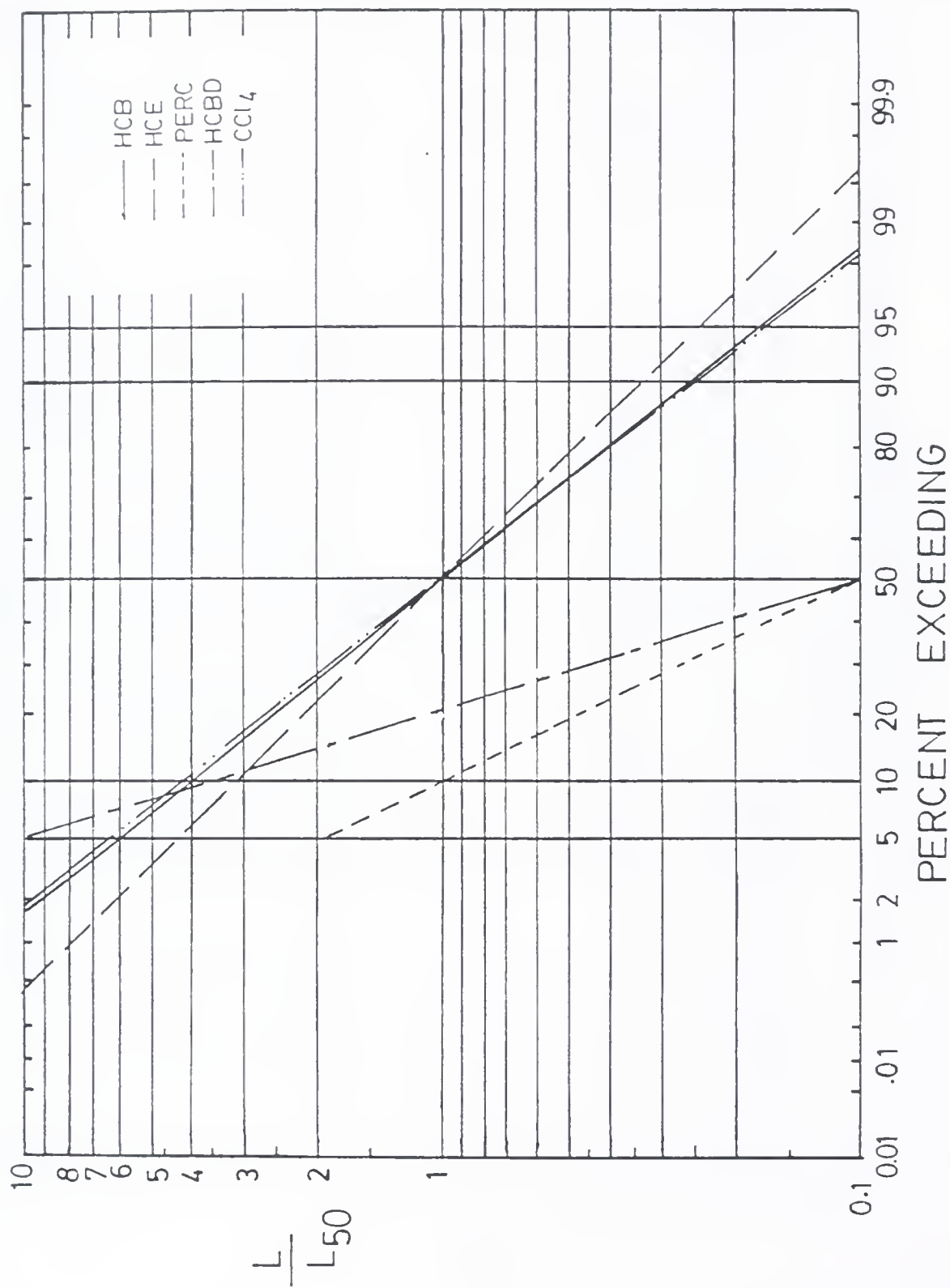


FIGURE 6.5.7: Normalized Load Frequency Curve for the Dow  
4th street sewer for HCB, HCE, PERC, HCB, HCE, PERC  
CCL<sub>4</sub>

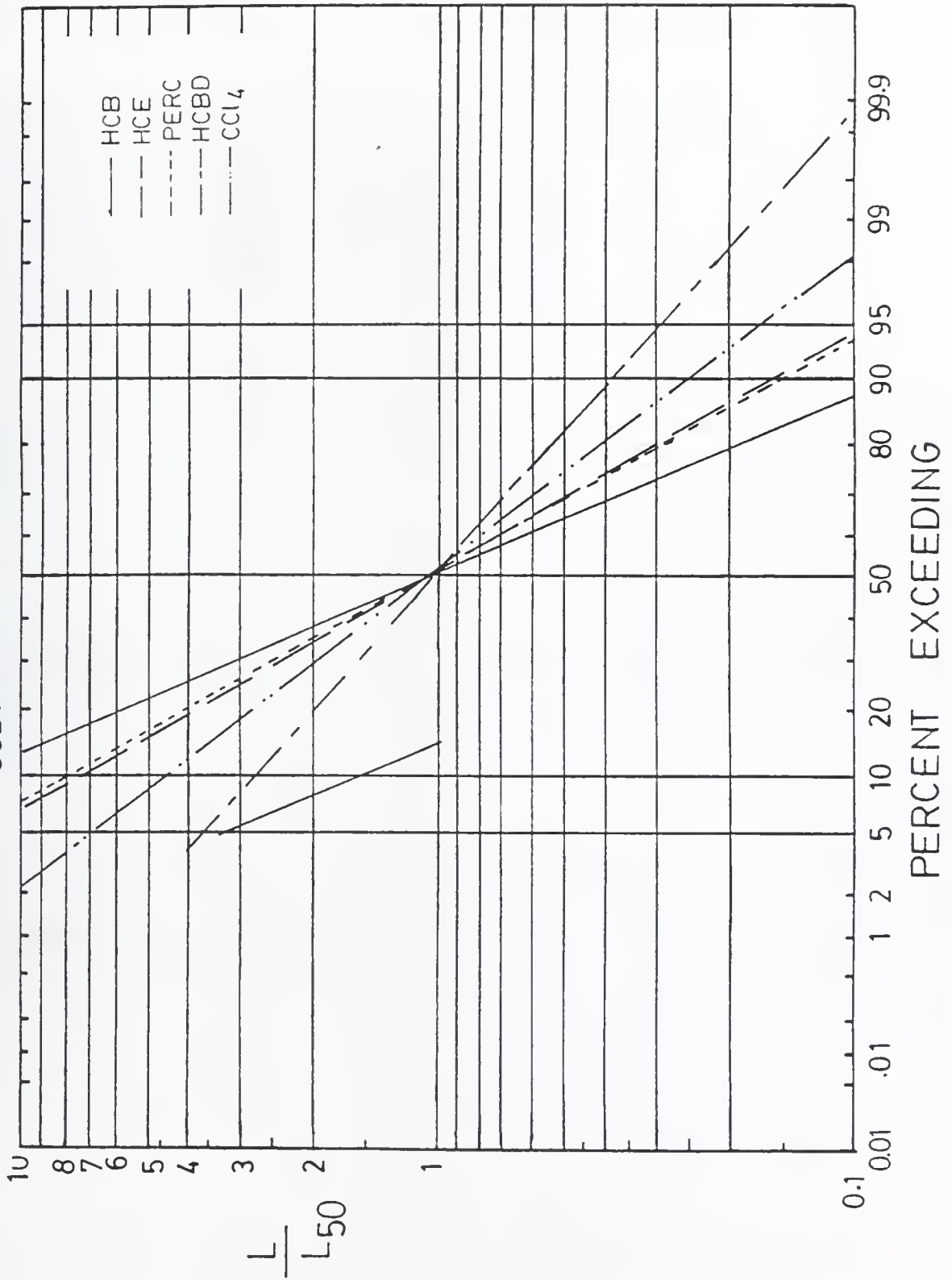
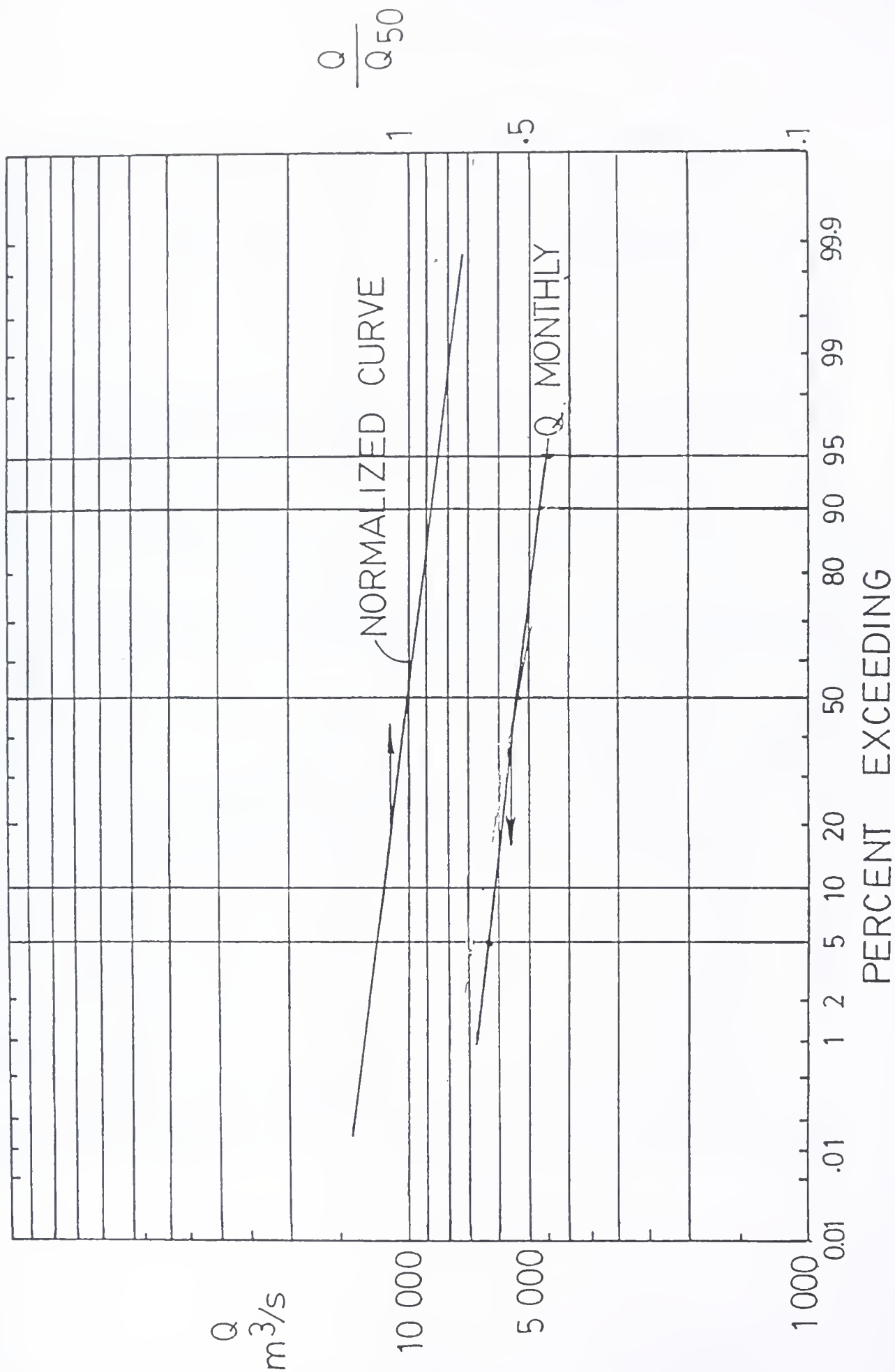




FIGURE 6.5.8: Flow Frequency Curve for the St. Clair River



$$\frac{Q}{Q_{50}}$$

1

.5

.1

$Q$   
 $\text{m}^3/\text{s}$

10 000

5 000

1 000

0.01

0.1

1

2

5

10

20

50

80

90

95

99

99.9

NORMALIZED CURVE

$Q$  MONTHLY

PERCENT EXCEEDING

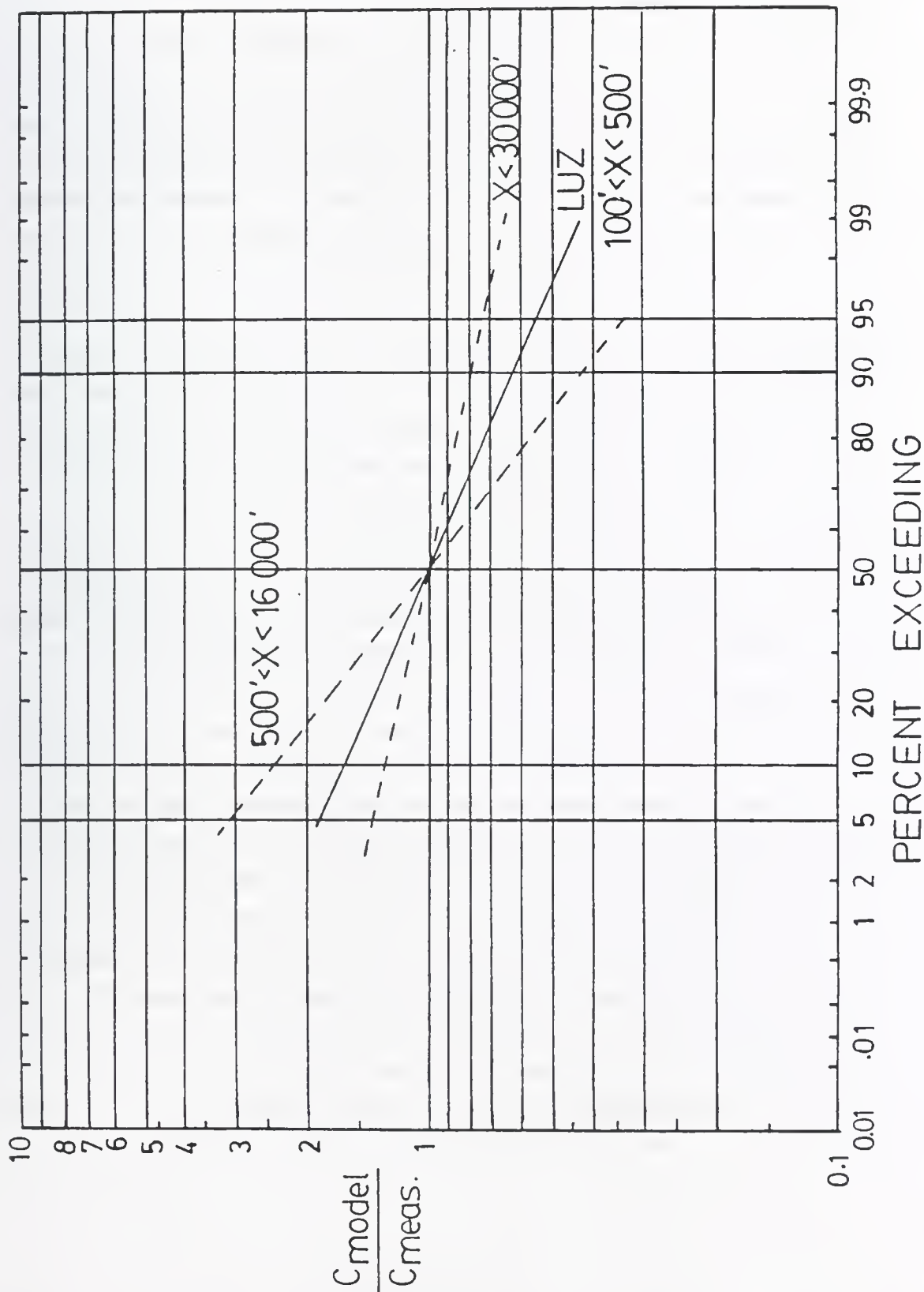


FIGURE 6.5.9: Calibration Error in KETOX

## 6.6. Load Allocation Procedures

### 6.6.1 Water Based Load Allocation

The KETOX model was selected for the water quality based load allocation procedure because it permits a more refined individual treatment of the outfalls as well as faster turnaround time. For the purpose of assigning MZs for each outfall and hence allocation loads to achieve the water quality criteria within these mixing zones, the KETOX model was run for the whole river with the long-term effluent loads for HCB (Section 4.1.1). This output showed that, for the reach from the Cole drain to Stag Island, the contaminants from the Cole drain, Dow Chemical and Polysar are concentrated in a stream tube of about 20% of the river flow as measured from the Canadian shore. A refined grid was then used in KETOX for the impacted portion of the reach from the Cole Drain to the end of the Suncor property (Figure 6.2.3). Load allocations for chemicals with water quality criteria will be presented for the outfalls in this reach.

In order to establish loads which will satisfy the water quality criteria within the above MZ restrictions, the outfalls were examined to determine the controlling restrictions. Table 6.2.1 shows calculations of the MZ for the major outfalls of the St. Clair River Pilot Site study. The computer programme (KETOX) was then run with the background concentration upstream of the first outfall. Several runs of the programme were made with various loads at the first outfall and a plot of concentration versus load was prepared for the controlling dimension ( $X_c$  or  $Y_c$  - Table 6.2.1). The loads were assigned as the median loads and the resulting graph represents concentrations that would be equalled or exceeded 50% of the time. Using the load frequency curve for the purpose of this modelling exercise, the calibration error of the model and the river flow variability, the 5% exceedence curve was also plotted. Using the water quality criteria (Table 6.4.1) for the chemical of concern and

the agreed level of exceedence for the purpose of this modelling exercise e.g. 5% exceedence (That is 95% of the months will be at or below the objective which represents 95% compliance) the load allocation curves were entered to obtain the required load. This load was assigned to Outfall # 1 (Cole drain) and the whole procedure was repeated for Outfall # 2 (Polysar, 72-inch). The procedure was repeated for all subsequent outfalls (Dow 1st St. complex (42-, 48-, 54-inch), Dow 2nd, Dow 3rd and Dow 4th Street). The loads obtained from this procedure represent the median monthly loads that must be maintained in order to meet a 95 % compliance within the specified MZ. The arithmetic average loads were 20 to 50% higher due to the log-normal nature of the distribution.

The above allocation procedure can be applied to all compartments of the ecosystem including the water column, bed sediment, and various food chain trophic levels. Separate analyses are required for each contaminant for which water quality objectives are available.

The load-frequency curves were developed assuming that the background concentration was zero; if the background concentration was not zero, then it was to be deducted from the water quality objective before entering the concentration-load curve for a particular outfall.

(a) Application

The allocation procedure will be illustrated using HCB as the parameter of concern. The provincial water quality objective (PWQO) for the water column for HCB is 6.5 ng/L. Criteria established by the New York State Dept. of Environmental Conservation and the U.S. EPA are respectively 330 ng/g for fish to protect piscivorous wildlife and 6.4 ng/g to protect human health based on average fish consumption levels. The background concentration in the St. Clair River obtained upstream of the Cole drain is between 0 and 0.1 ng/L. The first outfall with a significant HCB load is the Cole drain which discharges through an extended outfall into about 7.5 m. of water. Since this

plume may or may not be buoyant depending on the ambient temperatures, and since the outlet is at the bed the MZ limit was taken as the lesser of 4 times the depth or the distance to the next intake/outfall which is the Polysar intake. The distance to the Polysar intake is approximately 100m while 4 times the depth is 30m therefore, the  $X_c$  was taken to be 30m. Abdel-Gawad (1985) studied extended bottom outfalls and found that even under buoyant conditions, the plume would have a greater impact on the bed sediments than a surface plume; however, the dilution is more rapid for the extended outfall.

Figure 6.6.1 shows a plot of predicted concentration at the Cole drain versus load. For a given mean monthly load the concentration has a log-normal distribution. Figure 6.6.1 shows the concentrations at the edge of the MZ that are equalled or exceeded 50%, 10% and 5% of the time based on the observed average monthly loads. The background concentration is taken as 0.1 ng/L which must be deducted from the PWQO before the loads are obtained from Figure 6.6.1. Based on a PWQO of 6.5 ng/L, the 50% noncompliance load is 43 g/day while the 5% noncompliance is 3 g/day. The existing mean load is 8.9 g/day. Therefore a median monthly load of 3 g/day is recommended; the corresponding mean monthly load would be 3.9 g/d. Appendix 8 outlines steps in an interactive computer programme for the detailed calculations that are involved in establishing a load allocation curve such as Figure 6.6.1.

Figure 6.6.2 shows the load versus concentration plot for the Polysar outfall which is a 72-inch sewer located approximately 525m downstream of the Cole drain. The local depth for this outfall is approximately 6m and it is most probable that it will have a buoyant plume. Furthermore, the nearest downstream outfall is 275m away, therefore a restricted zone of 5 times the local depth is used in preparing Figure 6.6.2. Based on the PWQO of 6.5 ng/L, the 50% noncompliance load is 7.7 g/day while the 5% noncompliance median load is 0.55 g/day. The existing mean monthly load is 0.1 g/day. Therefore the existing average load of 0.1 g/day will comply with the PWQO at the defined MZ; however, the existing load should not be increased.

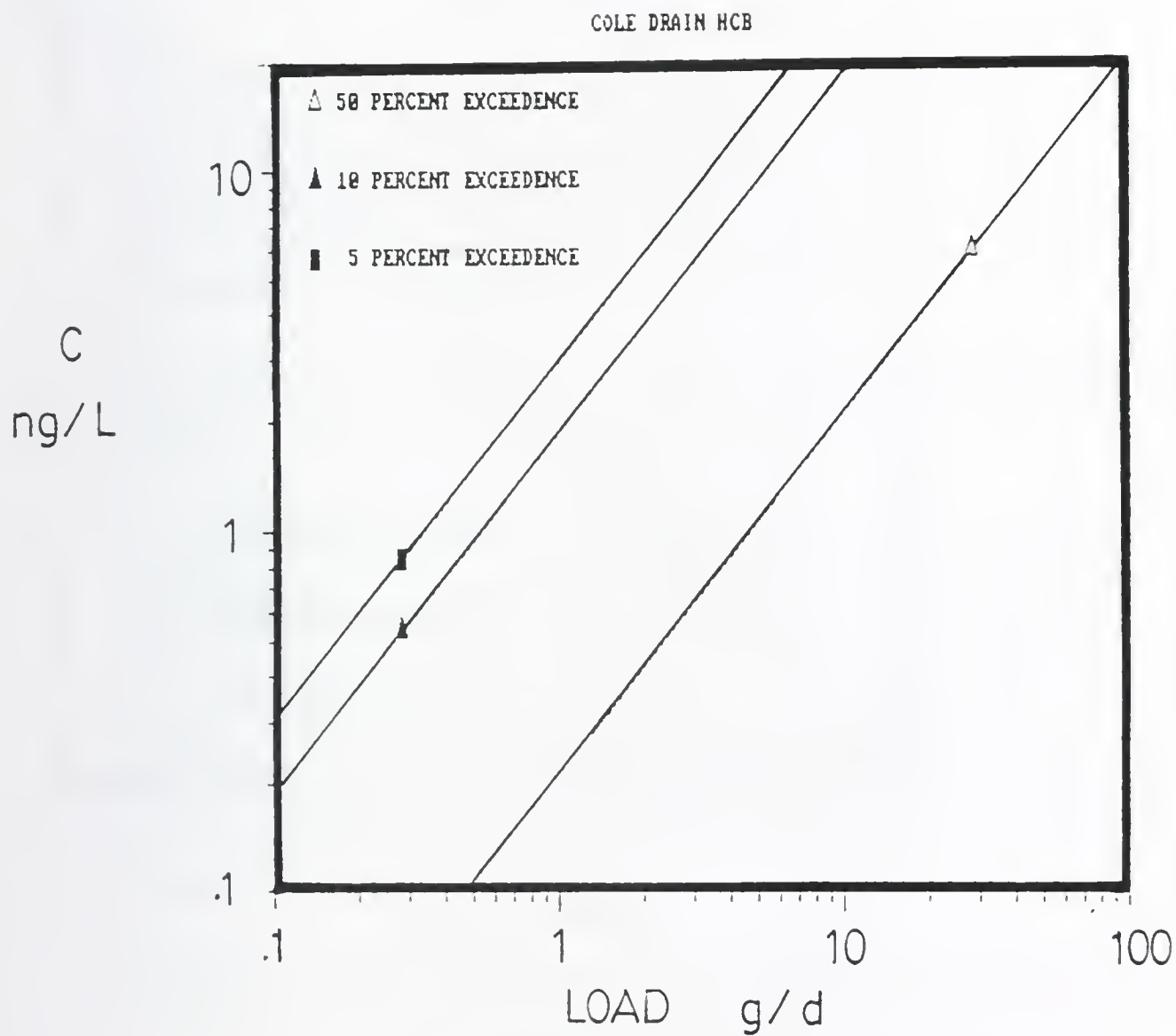


FIGURE 6.6.1: Cole Drain HCB Load Allocation for MZ-30m

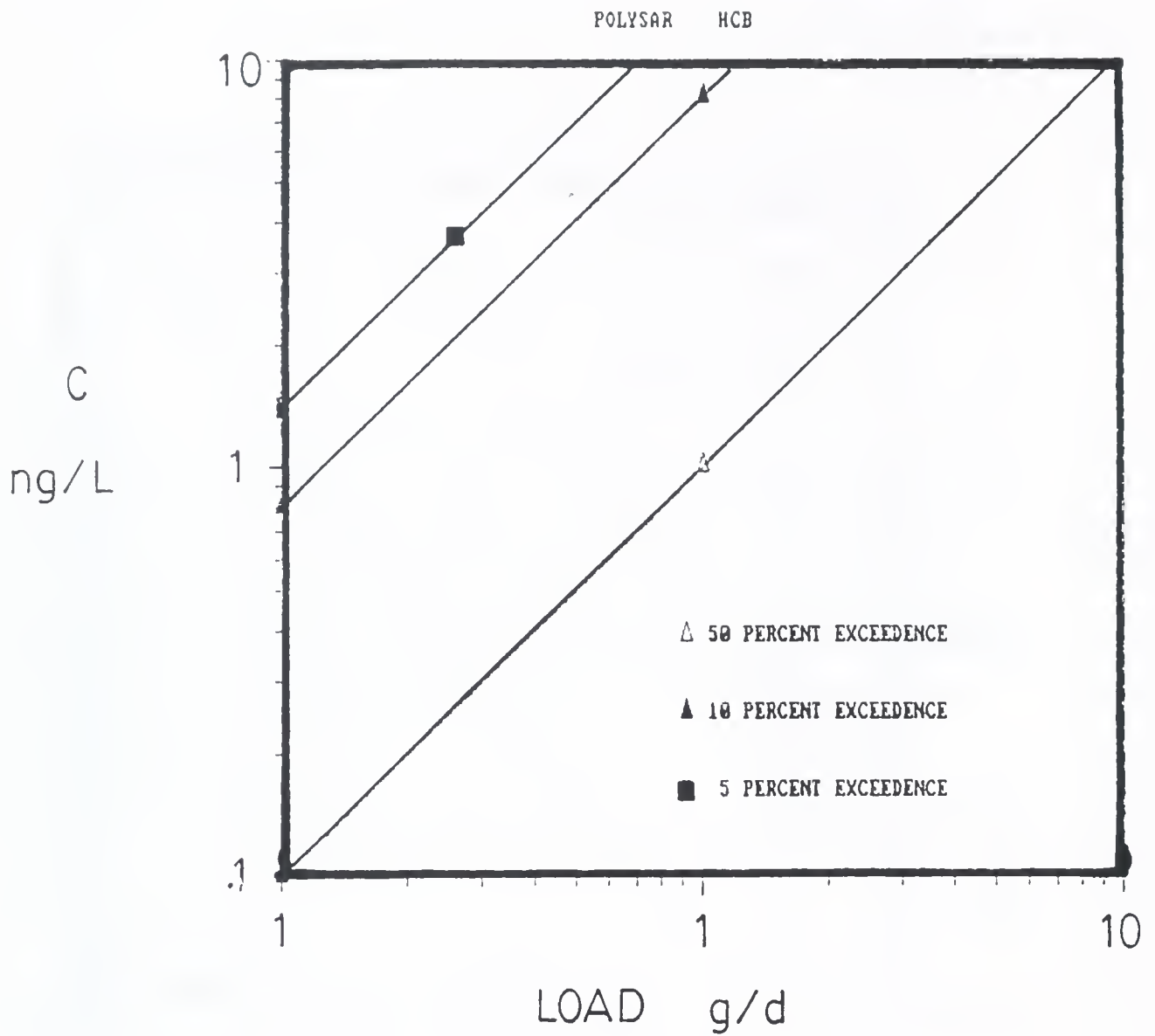


FIGURE 6.6.2: Polysar 72 inch HCB Load Allocation for  
MZ = 30m



Figure 6.6.3 shows the load versus concentration plot for the Dow 1st St. complex which includes all three sewers, namely the 42-, 48 and 54-inch pipes. The local depth for these outfalls is approximately 6m and it is most probable that they will have a buoyant plume for much of the year. The nearest downstream outfall is 300m away, therefore a restricted zone of 5 times the local depth is used in preparing Figure 6.6.3. Based on the PWQO of 6.5 ng/L, the 50% noncompliance load is 8 g/d while the 5% noncompliance median load is 1.4 g/day. The existing mean monthly load is 7.4 g/day. Therefore a mean monthly load of 1.7 g/day is recommended. This represents the summation of all three Dow 1st Street outfalls i.e. 42-,48-,and 54-inch.

Since there was insignificant HCB loads at the Dow 2nd and 3rd Street outfalls, these are not presented here. The current (1986-1987) load should be considered the maximum acceptable at this time.

Figure 6.6.4 shows the load versus concentration plot for the Dow 4th Street outfall. The local depth for this outfall is approximately 6m and it will have a buoyant plume for much of the year. The Suncor Property is about 300m downstream of this outfall; therefore a restricted zone of 5 times the local depth is used in preparing Figure 6.6.4. Based on the PWQO of 6.5 ng/L, the 50% noncompliance load is 9 g/day while the 5% noncompliance median load is 0.3 g/day. The existing mean monthly load is 3.3 g/day. Therefore a mean monthly load of 0.4 g/day is recommended.

Table 6.6.1 summarizes the water based HCB load allocations (Detailed water-based load allocations for additional chemicals are given in Appendix 9). It would appear that 95% compliance could be achieved if the load variability was decreased at the Cole drain, Dow 1st Street and Dow 4th Street outfalls.

The load allocation procedure outlined above can be used to assess the impacts of outfall configurations on the allowable loads. For example, the use of a diffuser would permit a higher load for the same MZ and the same load, flow, calibration variances; however, as will be

TABLE 6.6.1: WATER BASED LOAD ALLOCATION SUMMARY FOR HCB

WATER-KETOX AT EDGE OF MZ

QV(5%)=1.2; CV(5%)=1.8; PWQO = 6.5 ng/L

OUTFALL	LV(5%)	CS(5%)	BGD ng/L	EXISTING MEANS		ALLOCATED LOADS		
				L g/d	C ng/L	L50 g/d	L95 g/d	X95 g/d
COLE	13	14	0	8.9	2	43	3	3.9
COLE	13	14	.1	8.9	2.1	42	3	3.9
POLYSAR	13	14	0	0.1	0.1	7.7	.55	0.7
POLYSAR	13	14	.5	0.1	0.6	7.0	.55	0.7
DOW 1	5	5.7	0	7.4	7	8.0	1.4	1.7
DOW 1	5	5.7	1	7.4	8	6.0	1.1	1.3
DOW 2	11	12	0	-	-	-	-	-
DOW 3	5.8	6.6	0	-	-	-	-	-
DOW 4	32	34	0	3.3	3.1	9.0	0.3	0.4
DOW 4	32	34	1.5	3.3	4.6	7.0	0.2	0.3

(for legend see next page)

LEGEND FOR TABLE 6.6.1:

QV (5%) = ratio of 5% exceedence flow to median or median to a 95% exceedence;

CV (5%) = ratio of measured ambient concentration to modelled concentration when the frequency of exceedence is 5%, with known flow and load;

LV (5%) = ratio of the 5% exceedence load to the median load based on a monthly series;

CS (5%) = ratio of the ambient concentration that would be exceeded in 5% or less of the months to the model prediction when flows, loads and calibration errors are treated as independent random variables;

BGD = background concentration;

L = existing (1986-1987) mean load;

C = concentration;

L50 = median monthly load which should be allocated to ensure that in 50% of the months, the objective is met;

X95 = mean monthly load which should be allocated to ensure that in 95% of the months, the objectives will be met.

L95 = median monthly load which should be allocated to ensure that in 95% of the months, the objectives will be met.

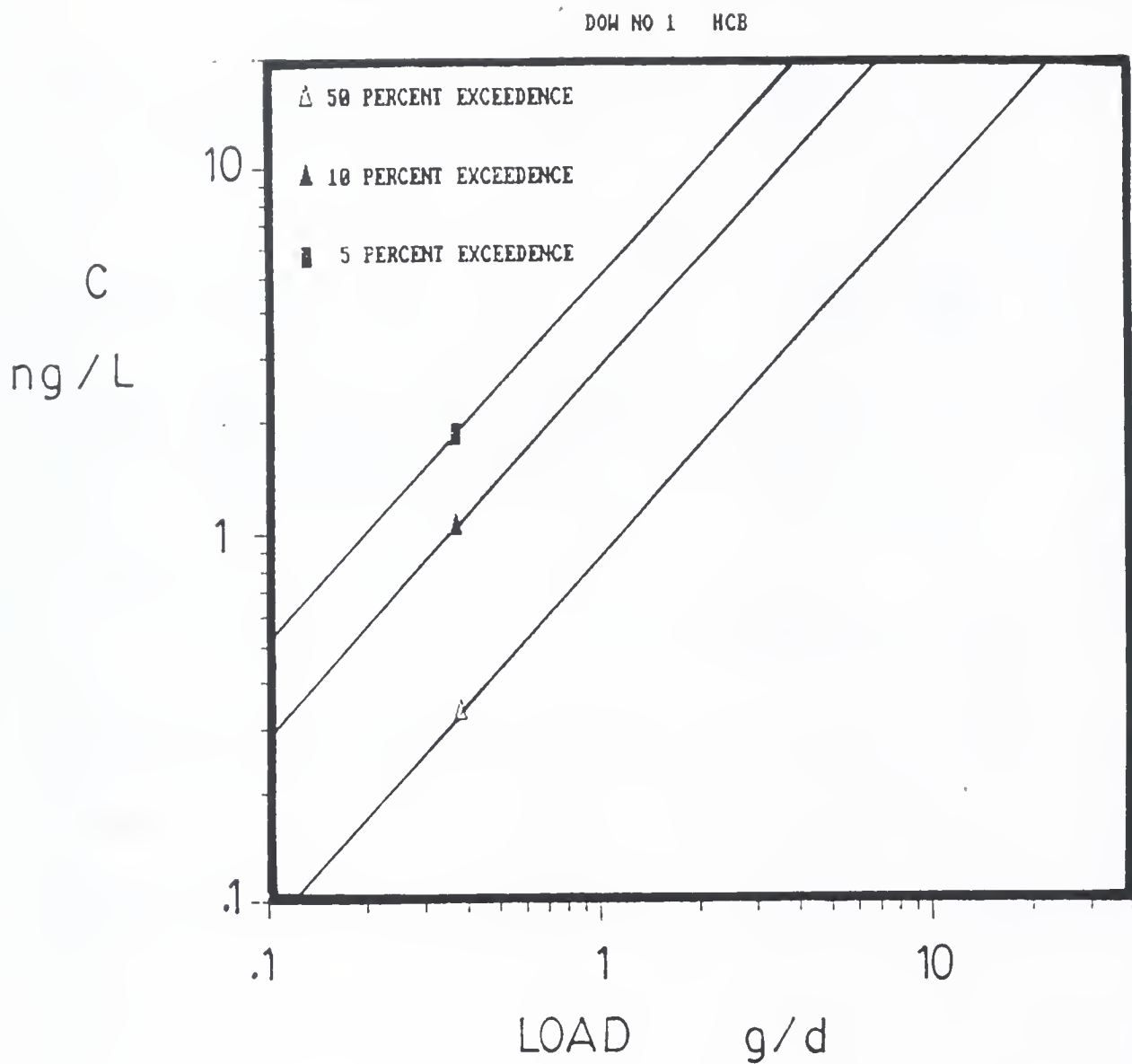


FIGURE 6.6.3: Dow 1st Street complex Load Allocation for  
MZ = 30m

DOW NO 4 HCB

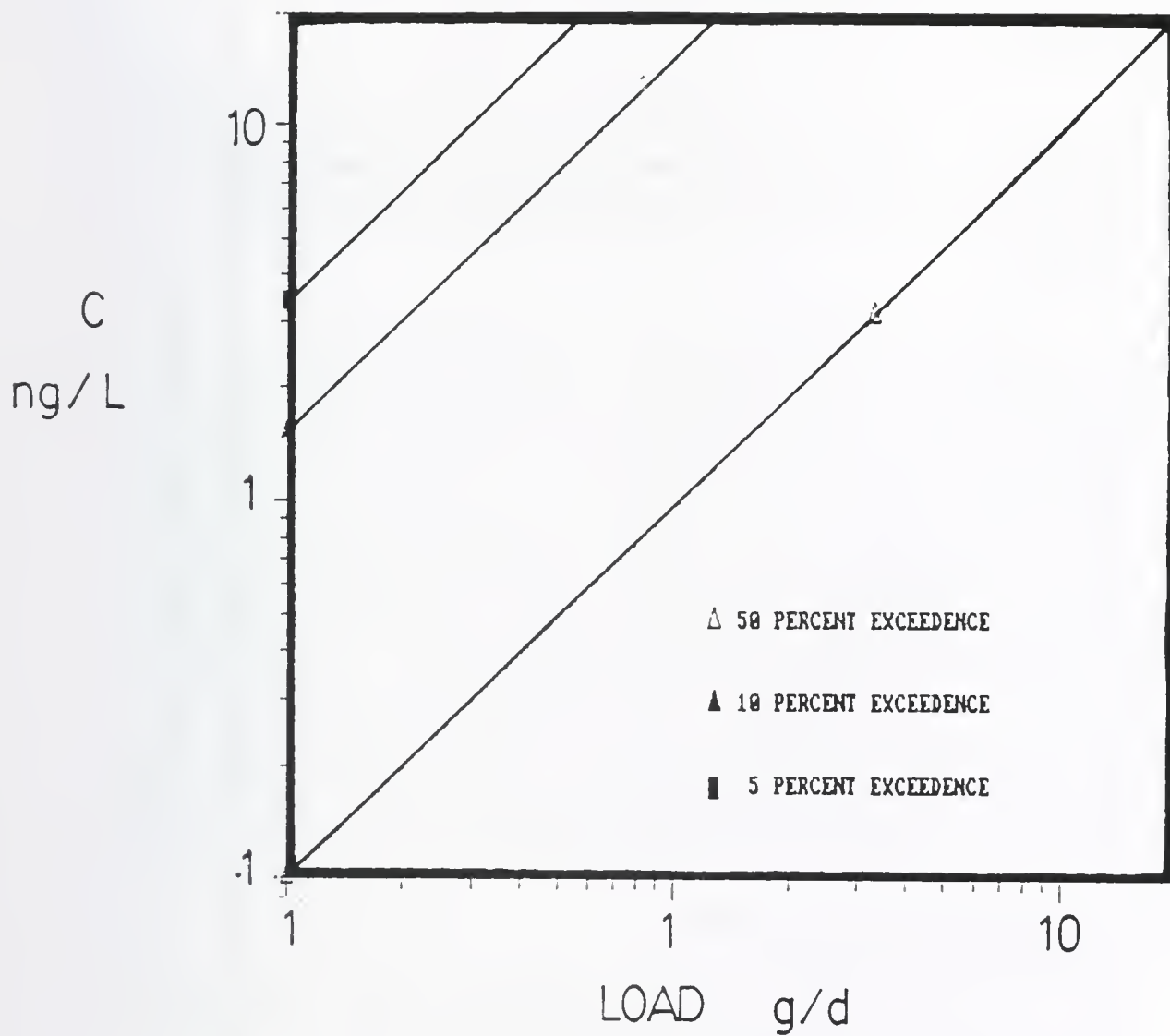


FIGURE 6.6.4: Dow 4th Street Load Allocation for  
MZ = 30m

discussed in the following section, these physical solutions may not satisfy ecosystem based water quality objectives. Moreover, these physical solutions must be regarded as short term solutions since in the long term, the objective will be zero or at least minimal mass discharge.

The effect of background concentrations was investigated and found to be relatively small for HCB in the example. The allocated mean monthly loads would be about 10% lower for the 95% compliance condition.

The KETOX model computes the equilibrium bed contaminant concentration; thus no contribution is made to the ambient concentrations in the water due to historical bed contaminants. WASTOX was run with the 1985 bed conditions (DOE/MOE 1986) and the 1986 loads; it was noted that the water concentrations in the lower river and in Lake St. Clair remained 25 to 50 percent above the equilibrium concentrations after 1/2 year. The reach of the river near the Dow site would respond much faster, e.g. a 25 percent elevation of concentrations near the bed may persist for 2 or 3 months; however, this would drop by half after 6 months. The contributions from bed sediments will not greatly effect these load allocations which were based upon river conditions near the Dow site.

#### 6.6.2 Biota Based Load Allocation

The refinement of food chain modelling has not as yet reached the stage where we can confidently allocate loads based on simulation. Model calibration on a site specific basis has not been possible due to a lack of necessary data. Partial calibration has been achieved by using data at intermediate trophic levels e.g. clams, juvenile fish and plankton. Figures 6.2.17 and 6.2.18 show comparisons of predicted and measured fish body burden for HCB and OCS. Figures 6.6.5 and 6.6.6 show comparisons for clams in Lake St. Clair. Figure 6.6.7 shows the calibration error frequency curve for biota in Mitchell's Bay.

LAKE St. Clair - WASTOX - HCB  
HCB Concentration in 'FREE' CLAMS/BENTHICS

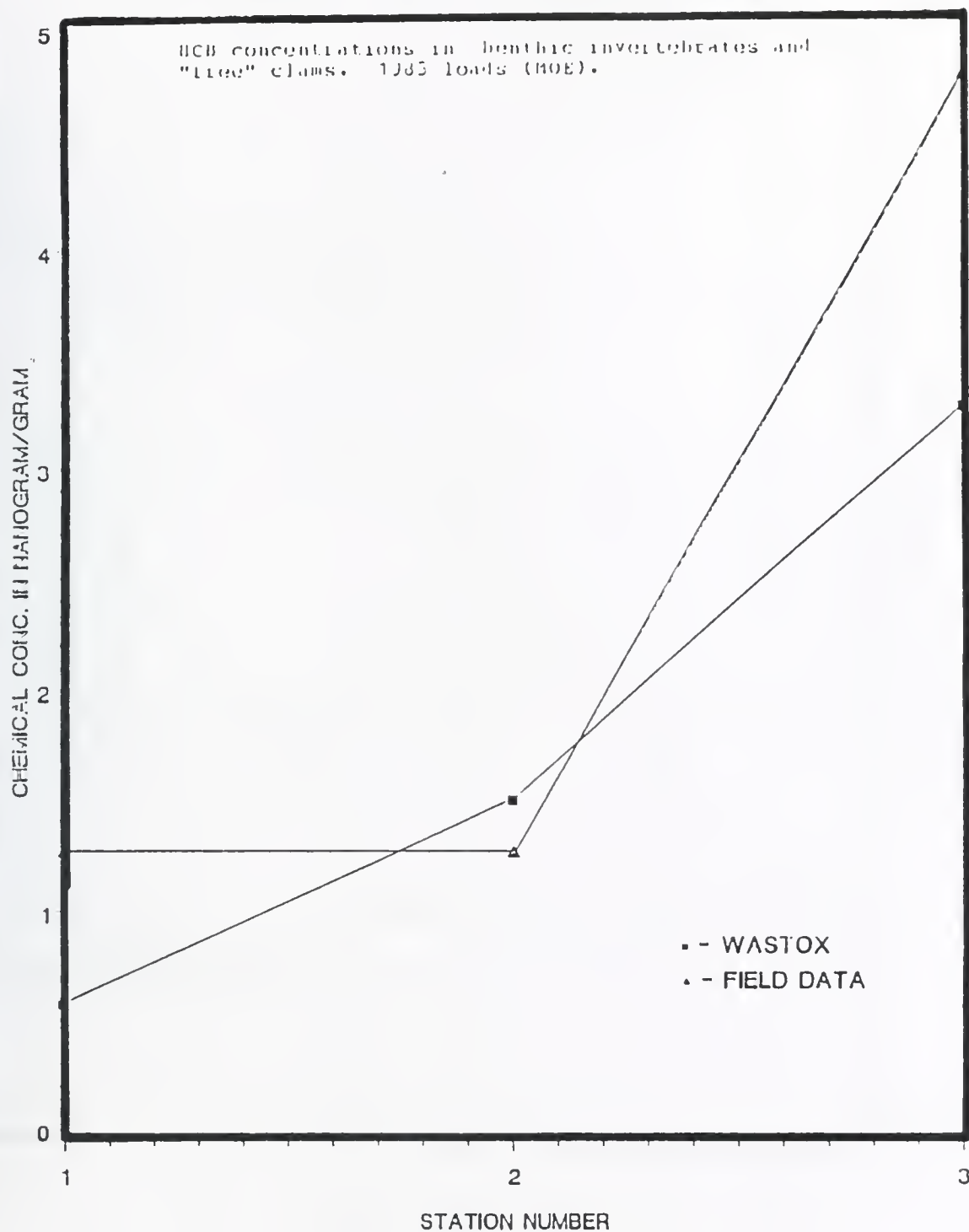


FIGURE 6.6.5: Predicted and Measured (GLI) HCB in Clams in Lake St. Clair [Sta. 1 South-East; Sta. 2 Mid-East; Sta. 3 South Channel Plume]



LAKE St. Clair - WASTOX - OCS  
OCS Concentration in 'FREE' CLAMS/BENTHICS

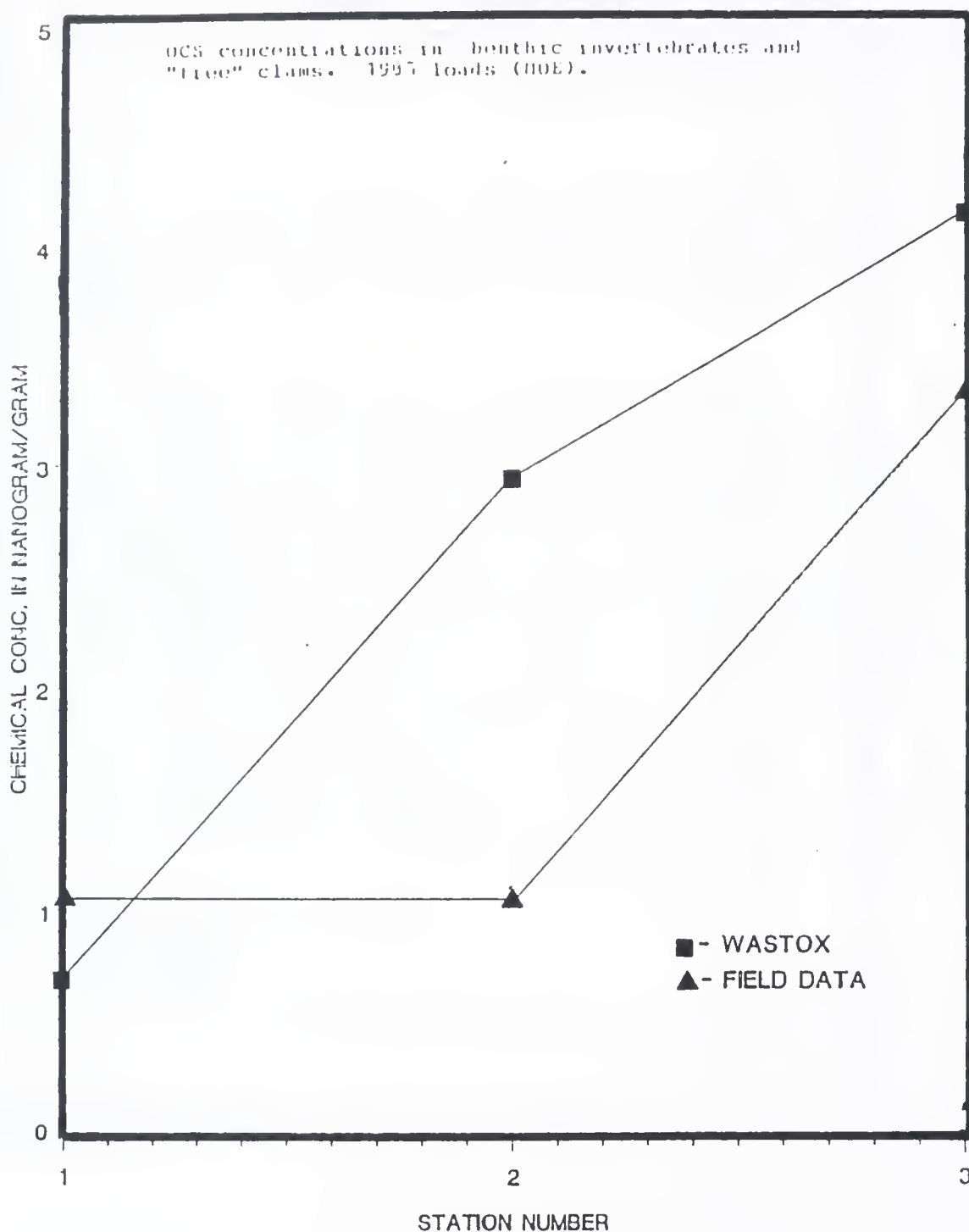


FIGURE 6.6.6: Predicted and Measured (GLI) OCS in Clams in Lake St. Clair [Sta. 1 South-East; Sta. 2 Mid-East; Sta. 3 South channel Plume]

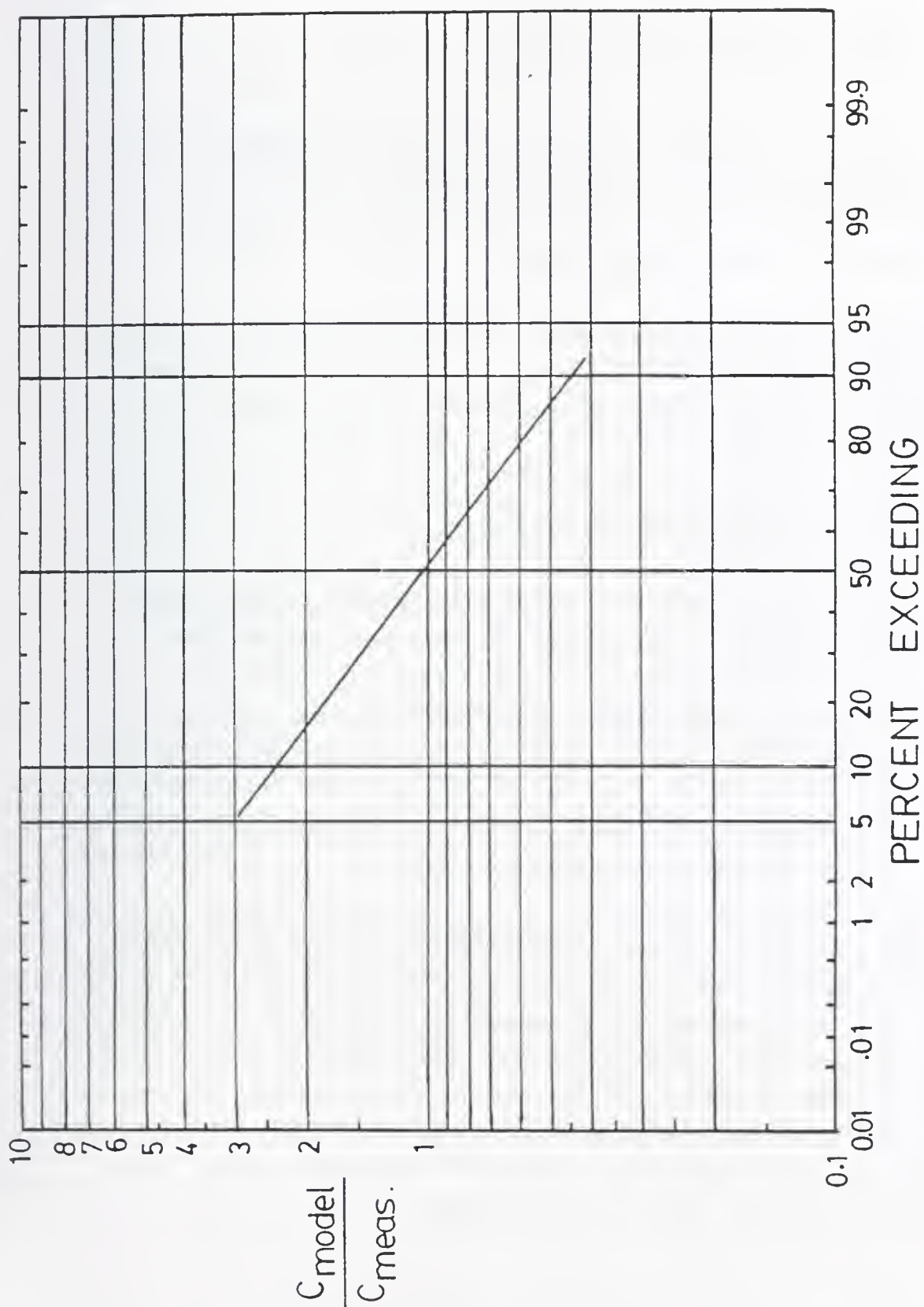


FIGURE 6.6.7: Calibration Error Frequency Curve for Biota Sub-Models.

As an indication of the future use of foodchain modelling in allocating loads to aquatic systems, the WASTOX model was applied to three microcosms of the St. Clair System. These are:

- (i) the zone containing 5% of the total flow adjacent to the Canadian shore between Polysar and Suncor;
- (ii) the zone containing 5% of the flow between Port Lambton and the Chenal Ecarte on the Canadian side of the river;
- (iii) Mitchell's Bay in Lake St. Clair.

The contaminant HCB was selected for illustration purposes. A guideline of 6.4 ng/g (wet weight) has been suggested by the U.S. EPA for the protection of human health. The guideline for protecting the aquatic ecosystem is 330 ng/g.

The modelling procedure used is as follows:

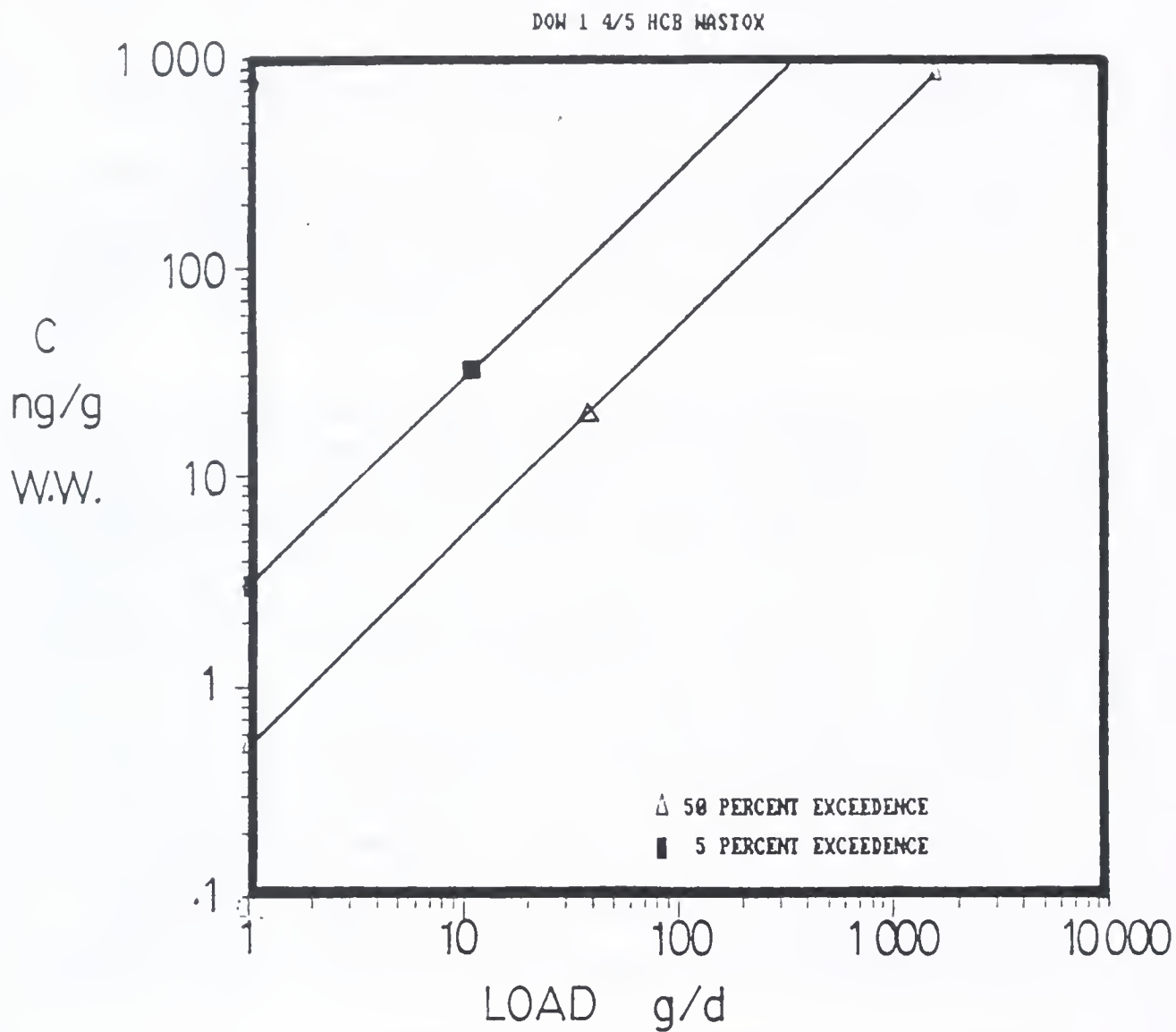
- (a) the exposure submodel of WASTOX was run with various loads to obtain exposure concentrations in the selected microcosms;
- (b) the food chain submodel of WASTOX which had been calibrated for Mitchell's Bay, was run for the exposure concentrations in (a);
- (c) load response curves were developed for each microcosm for the 50 and 95 percentile non-exceedence levels.

The WASTOX exposure model was run with 1985 bed concentrations for a period of 60 days with a constant point source load based on the twice weekly load distribution amongst the outfalls. The sixty day exposure concentrations were transferred to the TOXIWASP model to estimate the exposure levels in Lake St. Clair. The exposure levels at the Dow site, at Port Lambton, and at Mitchell's Bay in Lake St. Clair were treated as constant (steady state) inputs to the WASTOX food chain model. This food chain model was run as an unsteady model.

The model prediction was treated as the most probable or 50 percentile result while the 95 percentile was estimated by the same procedure used in the water column based load allocation. The calibration standard error in the food chain was estimated to be  $\pm 100\%$  based on data at different trophic levels at microcosm (i), (ii) and (iii). The standard error was taken to be the root mean square difference between the model and the biota data. Most of the comparative information was from Lake St. Clair. The mean monthly load frequency for the outfall with the dominant load and river flow frequency curves that were used in the water based load allocation were combined with the estimated calibration error in the food chain model to obtain the 95 percentile non-exceedence load-concentration curves.

Figures 6.6.8, 6.6.9 and 6.6.10 show the load response curves for microcosms (i), (ii) and (iii) for HCB. From these tentative results and using the EPA guidelines and 95% compliance on an average monthly basis the total average monthly load from the Dow complex should not exceed 2 g/d in order that fish in microcosm (i) be safe for human consumption. The corresponding load for the entire Canadian shoreline to protect the Chenal Ecarte microcosm [Port Lambton] (ii) is 20 g/d. The total mean monthly load for the entire river as well as other sources entering eastern Lake St. Clair should not exceed 200 g/d. Using the guidelines for aquatic wildlife (330 ng/g), the total load from the Dow Complex could be as high as 10 kg/d for 95% compliance for the Lake St. Clair microcosm. The present mean monthly loading is on the order of 12 g/d from the Dow site. The water column based guideline would reduce the combined load to a monthly median of 3.9 g/d (mean monthly approximately 5.0 g/d) from the Cole drain, Polysar, and Dow Chemical.

Since the Thomann food chain model was calibrated to agree with the steady state results of WASTOX the same calibration error is assumed to apply. The Thomann model used in conjunction with the KETOX model can determine the relationship between load and body burden at the edge of the MZ for each outfall. This is a rather "conservative" constraint; however, it assures that individual outfall impacts are not excessive. For consistency, a 5 percent non-compliance for



**FIGURE 6.6.8: Body Burden Response Curve for HCB in Adult Sport Fish near Dow Chemical**

PORT LAMBTON WASTOX HCB

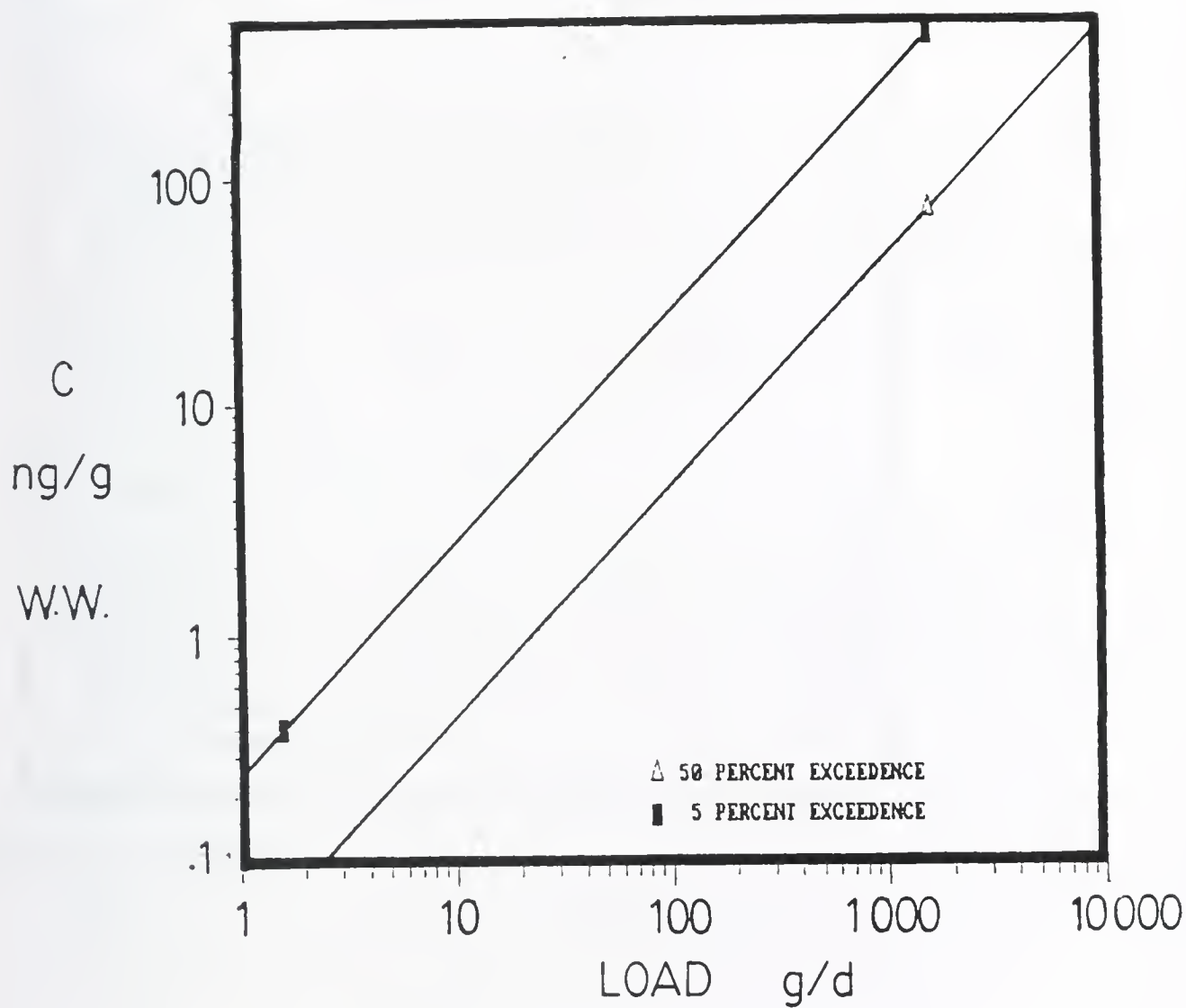


FIGURE 6.6.9: Body Burden Response Curve for HCB in Adult Sport Fish near Port Lambton

LAKE ST CLAIR WASTOX HCB

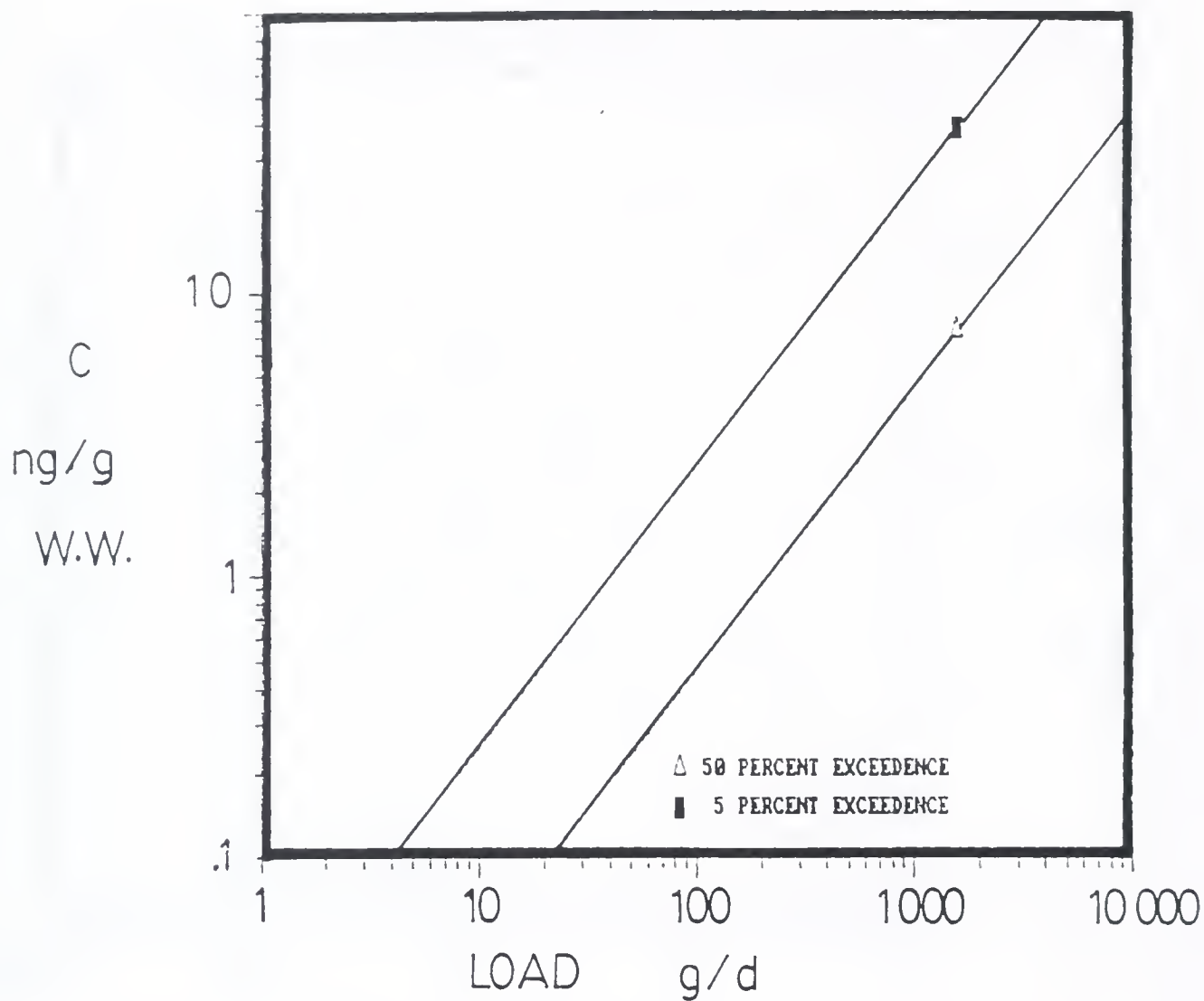


FIGURE 6.6.10: Body Burden Response Curve for HCB in Adult Sport Fish Mitchell's Bay, Lake St. Clair



monthly loadings of HCB is used in the following example. The background for each outfall is taken as the Lake Huron level of 0.1 ng/L. All of the chemical in the water column is assumed to be bioavailable. Figure 6.6.11 shows the biota based load allocation curve for the Dow 1st Street Sewer Complex based on the KETOX-Thomann model.

The load allocation results are summarized in Table 6.6.2. For illustration purposes the findings for the Dow 1st Street Sewers are discussed here. The existing median monthly load is 6.9 g/d (mean load 7.4 g/d) which gives a 50 percent non-compliance body burden of 60 ng/g. In order to satisfy the criterion of 330 ng/g 95% of the time, the median load will have to be less than 5.7 g/d. Detailed biota based load allocations, for the parameters of concern and for various objectives are shown in Appendix 9.

### 6.6.3 Sediment Based Load Allocation

The discussion in this section must be qualified as being tentative due to the high uncertainty in the model calibration. Currently, sediment criteria have only been set for HCB. Figure 6.6.12 shows a comparison of the WASTOX prediction with MOE sediment measurements obtained in 1985 (DOE/MOE 1986). The dynamic nature of the bed during 1986 made it extremely difficult to use these data for calibration. The calibration was therefore based on the 1985 loads and sediment survey. HCB and OCS were selected for the calibration. Figure 6.6.13 shows a tentative calibration error frequency curve for the 1985 bed data. The time response for the bed near the Dow site is on the order of 2 months, therefore it is assumed that the mean monthly load and river flow frequency curves can be applied to yield a worst case estimate for the load allocation.

Figure 6.6.14 shows the concentration of HCB on bed sediment as a function of load from the Dow 1st Street Sewer and exceedence level. All other loads upstream of this outfall are assumed zero. Applying the bulk sediment guideline of 80 ng/g, the 50 percent non-exceedence mean load is 2.7 g/d while the 95 percent non-exceedence mean is

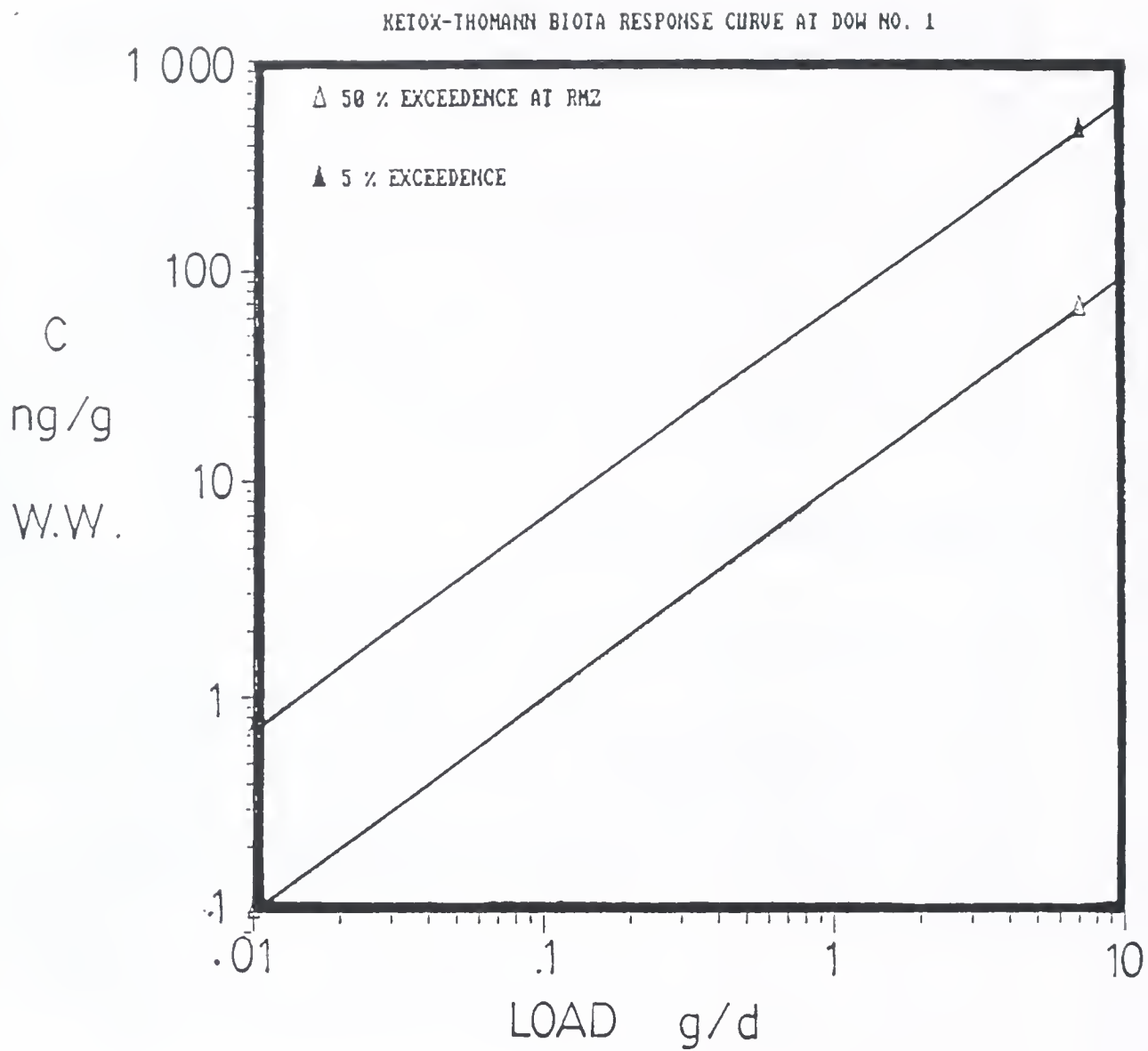


FIGURE 6.6.11: KETOX-Thomann Model for Biota Based Load Allocation for HCB at the Dow 1st. Street Sewer Complex

TABLE 6.6.2: BIOTA BASED LOAD ALLOCATION SUMMARY FOR HCB

KETOX-THOMANN: QV(5%)= 1.2; CV(5%) = 3.0; PWQO = 330 ng/g

OUTFALL	LV(5%)	CS(5%)	BGD ng/g	EXISTING MEANS		ALLOCATED LOADS		
				L g/d	C ng/g	L50 g/d	L95 g/d	X95 g/d
COLE	13	16.3	0	8.9	16	240	14	20
COLE	13	16.3	1	8.9	17	240	14	19
POLYSAR	13	16.3	0	0.1	1	50	3	3.6
POLYSAR	13	16.3	5	0.1	6	50	3	3.6
DOW 1	5	7.1	0	7.4	60	43	6	7.8
DOW 1	5	7.1	9	7.4	69	43	6	7.6
DOW 2	11	26	0	-	-	47	4	4.2
DOW 3	5.8	18	0	-	-	40	5	6.0
DOW 4	32	38	0	3.3	26	43	1	2.0
DOW 4	32	38	14	3.3	39	42	1	1.9

LEGEND FOR TABLE 6.6.2:

QV (5%) = ratio of 5% exceedence flow to median or median to a 95% exceedence;

CV (5%) = ratio of measured ambient concentration to modelled concentration when the frequency of exceedence is 5%, with known flow and load;

LV (5%) = ratio of the 5% exceedence load to the median load based on a monthly series;

CS (5%) = ratio of the ambient concentration that would be exceeded in 5% or less of the months to the model prediction when flows, loads and calibration errors are treated as independent random variables;

BGD = background concentration;

L = existing (1986-1987) mean load;

C = concentration;

L50 = median monthly load which should be allocated to ensure that in 50% of the months, the objective is met;

X95 = mean monthly load which should be allocated to ensure that in 95% of the months, the objectives will be met.

L95 = median monthly load which should be allocated to ensure that in 95% of the months, the objectives will be met.

0.1 g/d. Based on these data it would appear that the sediment criterion will be met if the water concentration criterion, (as shown in Table 6.6.1) is satisfied.

A summary of the sediment based load allocation is presented in Table 6.6.3.

TABLE 6.6.3: SEDIMENT BASED LOAD ALLOCATION SUMMARY FOR HCB

WASTOX: QV(5%)=1.2; CV(5%)=14.0; PWQO =80 ng/g

OUTFALL	LV(5%)	CS(5%)	BGD ng/g g/d	EXISTING MEANS		ALLOCATED LOADS		
				L	C	L50 g/d	L95 g/d	X95 g/d
COLE	13	40	0	8.9	2.3	310	7.8	10
COLE	13	40	100	8.9	102	0	0	0
POLYSAR	13	40	0	0.1	1	80	2	2.6
POLYSAR	13	40	100	0.1	100	0	0	0
DOW 1	5	22	0	7.4	8	74	3.3	4.
DOW 1	5	22	200	7.4	208	0	0	0
DOW 4	32	78	0	3.3	4	66	0.8	1.2
DOW 4	32	78	200	3.3	204	0	0	0

LEGEND FOR TABLE 6.6.3:

QV (5%) = ratio of 5% exceedence flow to median or median to a 95% exceedence;

CV (5%) = ratio of measured ambient concentration to modelled concentration when the frequency of exceedence is 5%, with known flow and load;

LV (5%) = ratio of the 5% exceedence load to the median load based on a monthly series;

CS (5%) = ratio of the ambient concentration that would be exceeded in 5% or less of the months to the model prediction when flows, loads and calibration errors are treated as independent random variables;

BGD = background concentration;

L = existing (1986-1987) mean load;

C = concentration;

L50 = median monthly load which should be allocated to ensure that in 50% of the months, the objective is met;

X95 = mean monthly load which should be allocated to ensure that in 95% of the months, the objectives will be met.

L95 = median monthly load which should be allocated to ensure that in 95% of the months, the objectives will be met.



St. Clair RIVER - WASTOX - HCB  
HCB Concentration in BED

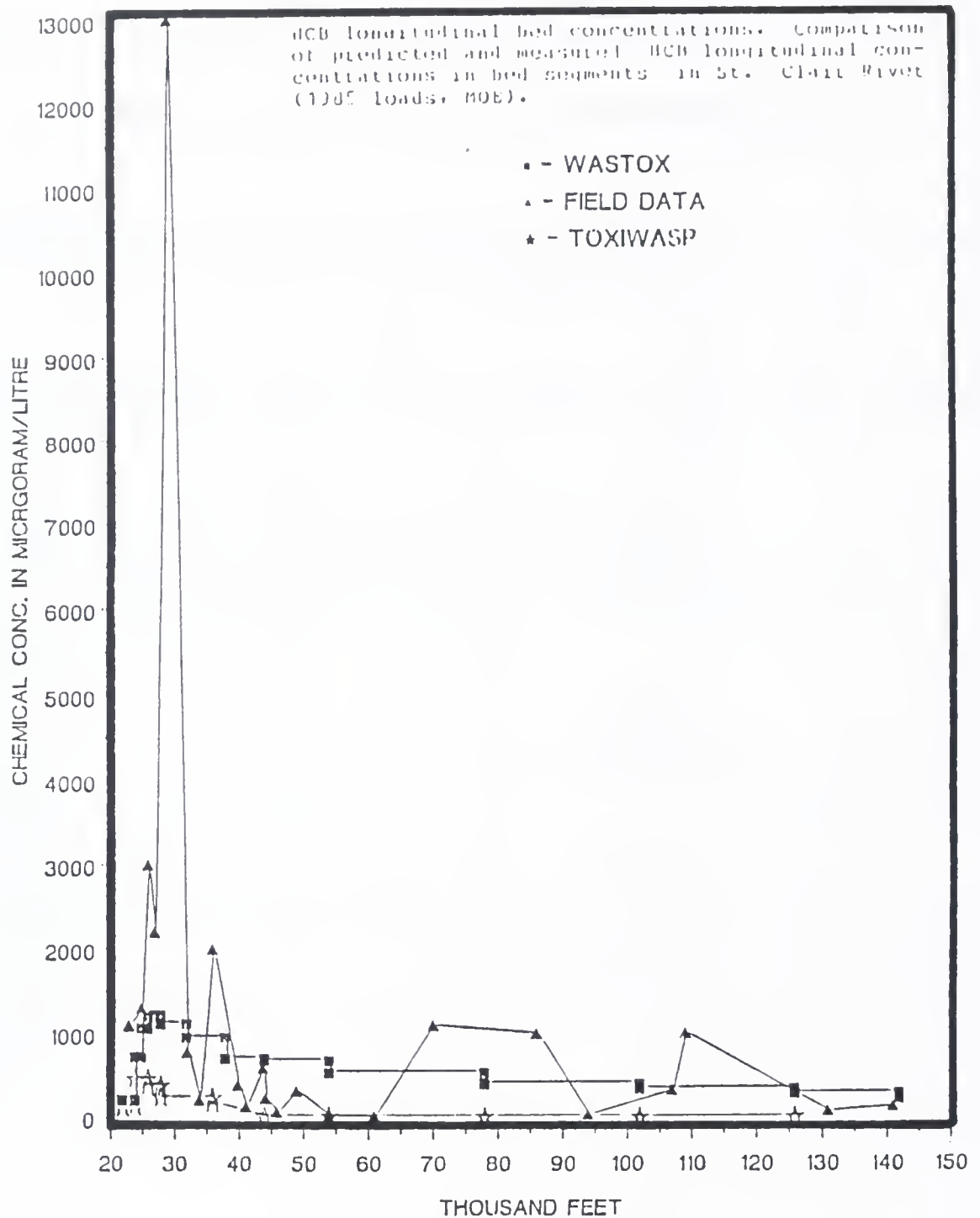


FIGURE 6.6.12: Comparison of the WASTOX Predicted and MOE Measured Bed Concentrations on Sediments for 1985 Loads

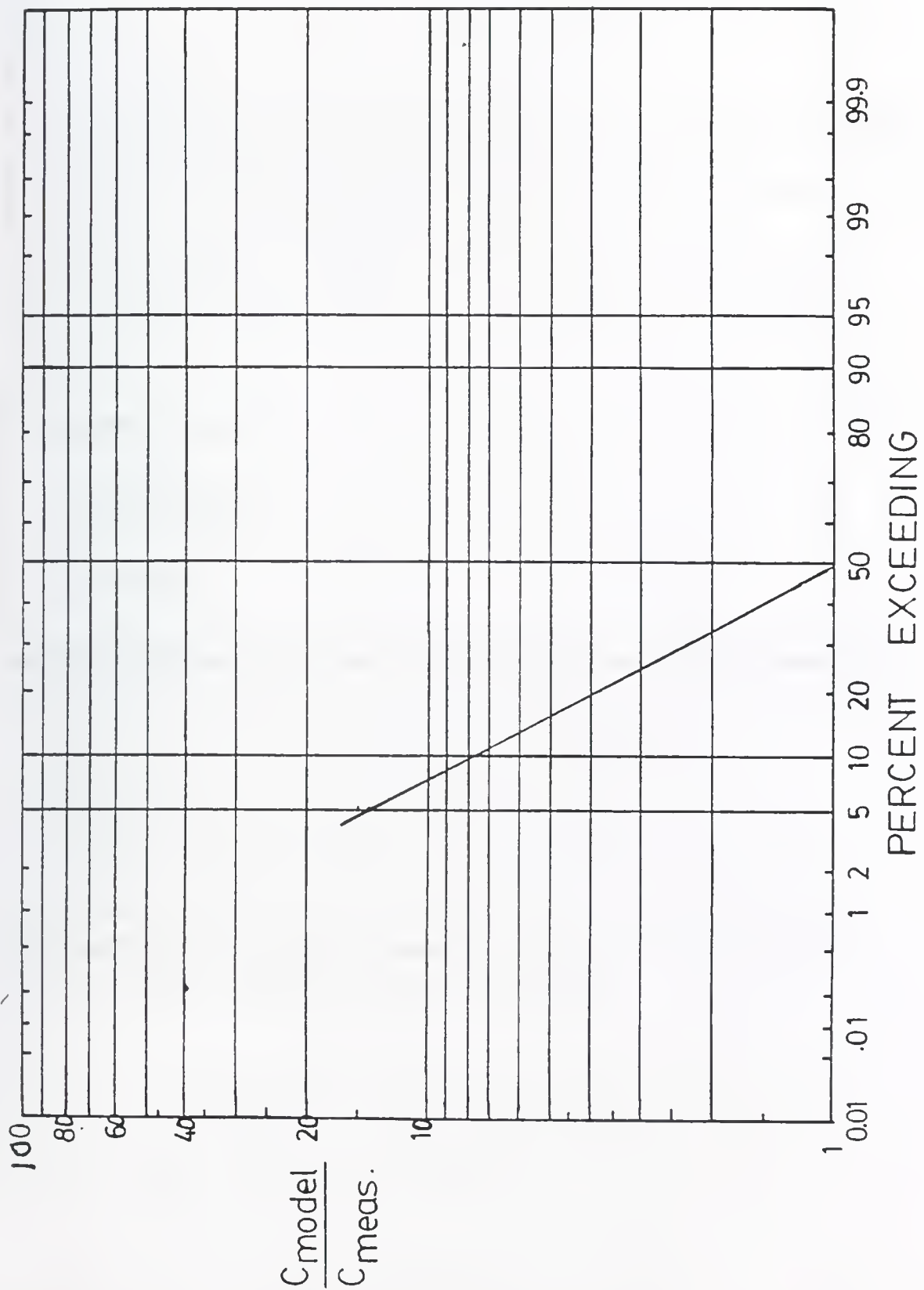


FIGURE 6.6.13: Calibration Error Frequency Curve for the Sediment System for HCB Based on 1985 Data

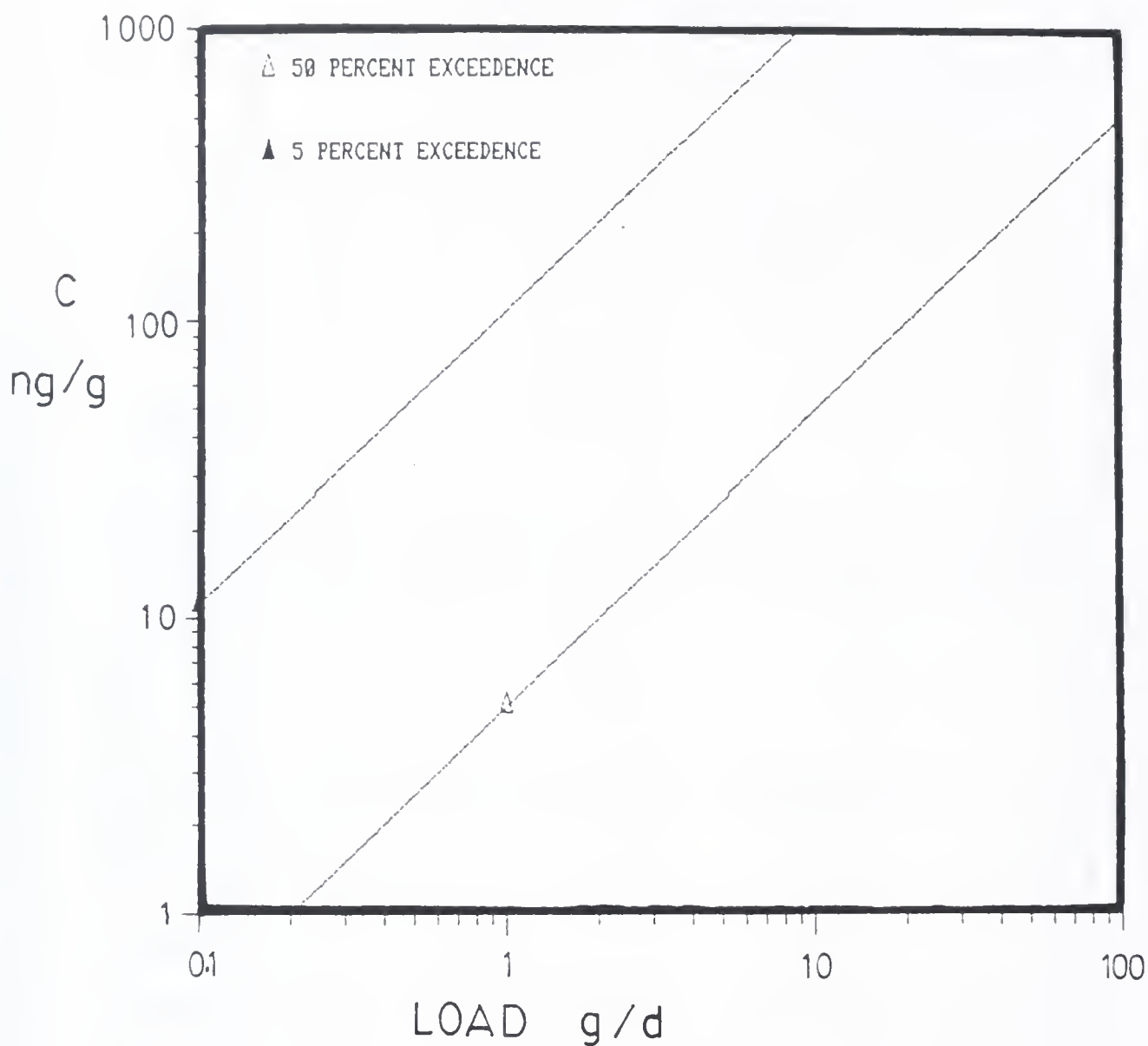


FIGURE 6.6.14: Sediment Contaminant-Load Frequency Curve for HCB at Dow 1st Street Sewer

0.1 g/d. Based on these data it would appear that the sediment criterion will be met if the water concentration criterion, (as shown in Table 6.6.1) is satisfied.

A summary of the sediment based load allocation is presented in Table 6.6.3.

By comparing the load allocation results for water, biota and sediment (i.e. Tables 6.6.1, 6.6.2 and 6.6.3); it would appear that the combination of the EPA human health guideline for fish consumption and the limiting load to the Dow microcosm of 2 g/d will be the controlling criterion for the outfalls from Cole drain to Suncor for HCB. Appendix 9 shows the sediment based effluent load allocations for all of the outfalls.

## 6.7 Technique Assessment

### 6.7.1 Model Development

#### (1) Effort Required

The KETOX model developed in this study can be implemented on any IBM or compatible microcomputer. The implementation and testing requires about one man day for use on the same river system. Application to another river would require one to ten days depending on the complexity of the river. A two day training period is also recommended. Once the model has been implemented, a calibration procedure is required. If the load and ambient data are already assembled and well organized, the model can be calibrated in one or two weeks per contaminant. An additional one or two days should be reserved for verification of each contaminant.

The WASTOX model requires some specialized training. The exposure submodel of WASTOX requires about twice as long as KETOX to apply. The application of the food chain component of WASTOX requires a similar effort to the exposure submodel.

Recently the U.S. EPA (Ambrose et al. 1988) released WASP4 which incorporates many of the features of WASTOX. WASP4 has all the advantages of the WASTOX exposure submodel, as well as the capability of simulating conventional parameters (dissolved oxygen, total phosphorus and biological oxygen demand).

Ultimately it is expected that WASP4 will supersede WASTOX. It is expected that the calibrated WASTOX files can be modified for execution by WASP4.

The Thomann four trophic level steady state food chain model can be implemented and used after a few minutes of explanation.

## (2) Equipment Needed

The KETOX model has been developed for a microcomputer (IBM-XT or AT or compatible) with a math co-processor. The complete St. Clair River can be simulated in 20 minutes. The WASTOX exposure model will run on an AT microcomputer with 640K RAM and a 20 MB hard disk; however, the execution time for the St. Clair River was excessive; more than 8 hours was required to obtain information on the bed sediment response. It is recommended that WASTOX be implemented on a mainframe to improve turn around time.

The WASTOX food chain can be run separately from the exposure model. Simulations representing several years of biotic activity can be completed in approximately one hour on an AT microcomputer.

## (3) Staff Expertise

All the models require involvement of or supervision by staff with backgrounds in environmental modelling, river mechanics and aquatic biology.

#### (4) Data Considerations

The WASTOX and KETOX models generate large data files which require processing in order to use the information in decision making. The output from both models can be processed by spread sheet software such as LOTUS<sup>TM</sup> to produce graphical output. Some screen graphics have been developed for the KETOX model.

#### (5) Technology Transfer

The MOE has on staff the expertise to use all of the proposed models. Many of the affected industries have environmental engineers (civil and chemical engineers) that could operate the KETOX model. The permittee may require the assistance of a consultant for the initial application. The Thomann food chain could be used by a permittee. In most cases a permittee, e.g. a municipality would require assistance from MOE or a consultant in using the WASTOX model.

### 6.7.2 Interpretation of Model Results

#### (1) Staff Requirements

The interpretation of model results should not be done by the modeller alone. The modeller can indicate the probable errors in output based on load variability, flow variability and calibration error. The modeller can also examine the output for stability and convergence problems. However, experts in areas such as biology and geochemistry will need to be involved in assessing the success of the model in duplicating these processes.

#### (2) Resources Needed

Softwares such as LOTUS<sup>TM</sup> or SYMPHONY<sup>TM</sup> would be useful in examining the output files from KETOX and WASTOX.

### (3) Reliability of Results

The reliability of predicted exposure concentrations depend mainly on the river flow variability, the load variability and the calibration errors for the model. The latter has been estimated and is presented in this report (Figure 6.5.1). River flow variability is the least important source of error. Load estimation due to the highly random nature of the loads is the greatest source of discrepancy between model and field results. Other errors may arise due to wind generated cross-currents and buoyancy effects near outfalls. Future field effluent studies should report effluent and ambient temperatures.

The WASTOX food chain model although subject to a large calibration error, is a useful tool in predicting the response of biota to changes in loads.

#### 6.7.3 Technique Utility Within MISA

##### (1) General Usefulness

The models developed in this study are designed for the Great Lakes connecting channels. These could be adapted to other large rivers. In addition to the St. Clair River, the KETOX model has already been applied to the St. Marys River, The Detroit River, the Niagara River and to the St. Lawrence River. The RIVMIX model of the CCIW, from which KETOX was developed has been applied to other rivers. The WASTOX model may, after some calibration, be applied to most parts of the Great Lakes System.

##### (2) Worst Case Conditions

Worst case scenarios can be examined with both of the proposed models. In fact, modelling is the only feasible way of studying hypothetical events representing extreme conditions.



(3) Conflicts

The models are to be used as a tool in assessment procedures. They are not intended to replace bioassay tests which indicate the effects of the integrated load of contaminants on organisms.

(4) Turn Around Time

Once calibrated for a river or lake system, results can be generated for specific permits in a few days.

(5) Utility in Meeting Pilot Site Criteria

(i) Both the KETOX and the WASTOX models can be used to allocate loads that should meet the criteria, for the water column. Their use for setting loads to meet sediment and biotic criteria must be regarded as tentative at this stage, i.e. the model can be used for preliminary estimates of load allocations but post-audit field data would be required to verify these load allocations. It is important to note that modelling is the only way in which hypothetical load-ambient concentration relations can be developed for specific contaminants; these relationships are essential for the allocation loads. Modelling is, therefore, an indispensable part of the Water Quality Track of MISA. The weaknesses alluded to in the biota and sediment components of the models are related to the complexity of these systems as well as the extensive data requirements for proper calibration and verification.

(ii) System Recovery

Both the KETOX and WASTOX models give estimates of the time responses in the various components in the system e.g. water, sediment and various trophic levels in the biota. The reliability of these has not been fully established but the results should be correct within an order of magnitude. Modelling is the only viable way of estimating the system recovery.

(iii) Point Source Versus Nonpoint Source

The models can identify the effects of individual point sources or diffuse sources. Thus, the model could indicate the potential benefits of treatment of point sources only.

(iv) Selection of Control Options

Since the models permit many different scenarios to be run, it is feasible to examine the relative benefits to be had from many control options.

(v) Baseline Assessment

One of the benefits of a good model is its capability to interpolate field data so that a more comprehensive picture of the system status is obtained. Thus, the optimal use is made of baseline data as well as monitoring data.

#### 6.7.4 Technique Applicability

(1) General Applicability

As noted earlier, the KETOX model was developed for large rivers such as the Great Lakes connecting channels. It is a steady state model. WASTOX, on the other hand, is a dynamic model and can be used in either lakes or rivers. Problems may be encountered in stratified lakes where special precautions are necessary in the cell selection and hydrodynamic input. With these restrictions both models can be used as screening tools. KETOX is better as a screening tool for rivers because it is easier to use and provides faster turn around times. Both models have similar accuracy of prediction for steady state loading conditions. It is suggested that KETOX and the Thomann Generic Food Chain Models or similar steady state models be used for screening purposes as well as for load allocation. The dynamic

models such as WASTOX are best used to study the unsteady behaviour of the system. The dynamic models can most efficiently be calibrated after the modeller has examined the steady state behaviour of the system with the use of simpler, fast turn-around models like KETOX.

## (2) Source of Information for Other Techniques

The hydrodynamics component of KETOX can be used for input to other models such as WASTOX, WASP4, and TOXIWASP. Also the flow distribution generated by KETOX can be used for discharge weighted mass flow calculations based on measured concentrations along a transect. The hydrodynamics and dispersion outputs are also useful in establishing both the spatial and temporal co-ordinates for sequential measurements in a river and determining possible depositional zones.

## (3) Site Specific Criteria

Water quality criteria are established based on observed or expected impacts; the models established in this study were set up to predict exposures and body burdens without regard to impact.

Once the impact criteria for water quality are established they can be used in the models to assess the current loads and/or determine the appropriate loads to meet the guidelines.

## (4) Discharger Use

The dischargers could use data from effluent self-monitoring as an input to either of the models to predict the current status of the receiving water. By using concurrent ambient water data the permittee could improve the reliability of the model by modifying such factors as the mass of in-place pollutants and the partitioning coefficients for the suspended and bed sediments.



## 7.0 CRITIQUE OF ASSESSMENT PROCEDURES

### 7.1 Critique of Component Studies From The Modelling Viewpoint

The development of contaminant fate and transport models requires a vast amount of field data in order to calibrate and verify the models. The models of this study had as an ultimate goal, the estimation or allocation of contaminant loads to meet environmental quality criteria. Since these criteria can be in terms of the whole water, sediment or in terms of body burden in a particular biotic species, both exposure and foodchain models were developed.

The various assessment techniques used in this study were themselves evaluated for their utility in establishing effluent limits. Table 7.1.1 provides a brief overview of the usefulness of the data generated for each technique, as well as the degree of effort expended in this study and the adequacy of this data for setting effluent limits.

#### 7.1.1 Effluent Monitoring

##### (a) Sequential Sampling

The sequential sampling (Section 4.1.3), with data collection at 1/2 hour intervals for 7 hours on 3 successive days on three separate cruises (spring, summer and fall 1986), revealed the highly random nature of the effluent loads and the river concentrations near the outfalls. These data were split into two groups; one group was used for calibration of the WASTOX exposure model while the other data were used for verification and estimation of the calibration error. The time averaged loads and the time averaged ambient concentrations were used to calibrate and verify the KETOX model in the reach from the Cole drain to Suncor. The sequential data also indicated the possibility that the ambient surface concentrations are affected by buoyancy of the effluent. Comparison of the three cruises indicated that this effect was most severe in the spring. The effect of buoyancy was to reduce vertical mixing with the result that surface

concentrations were greater than the depth averaged concentrations. In the future, these data will prove useful in testing and establishing statistically based monitoring procedures.

(b) Long-Term Effluent Monitoring

The long-term effluent monitoring programme assessed the loadings at selected major outfalls upstream of Suncor for an 11 month period. These data were useful in establishing mean monthly load frequency curves for these significant contributors. The KETOX model was used to relate these loads to the exposure concentrations in the river. Using load-response curves (concentration versus load) for the key outfalls and the expected load variability, river flow variability and the model calibration error, it was possible to assign compliance levels to the load response curves. These curves were then used to estimate the load that would give an acceptable exposure concentration (i.e. criteria) at an acceptable frequency level.

7.1.2 Ambient Monitoring

(a) Investigative Water Sampling

The investigative water sampling was used to verify both the WASTOX and KETOX models for the long-term loads represented by the long-term effluent data.

(b) Sediment Contaminant Distribution

The surficial sediment sampling was useful in (i) providing a better description of the bed material, (ii) providing information for the calibration of the particulate partitioning in both WASTOX and KETOX, and (iii) providing representative boundary conditions for the exposure models.

The extreme variability of the bed sediment composition and contaminant levels in the river made it difficult to calibrate this



component of either model. More data are necessary to complete the sediment calibration and the model results on sediment should be regarded as tentative at this time. The sediment data collected in 1986 were representative of a dynamic system since the 1986 loads for many of the contaminants of concern were much lower than the 1985 loads. Since the sediment system response time is on the order of one year it was difficult to associate the measured 1986 loads with the observed bed concentrations. The WASTOX model, for example, starting with 1985 bed conditions, indicated that the 1986 bed concentrations decreased with distance from the Dow site to Stag Island while they increased from Stag Island towards Port Lambton. A good calibration could not be obtained within the context of the above described dynamic behaviour. A tentative calibration was made based on the 1985 loads and bed concentrations. The 1986 data serve to confirm the order of magnitude of the response times estimated by the WASTOX and the KETOX models.

Field data indicate that contaminant concentrations in the bed sediment can vary by two or more orders of magnitude for stations that are subject to almost identical mean exposures; the differences can be partly attributed to differences in the physical and chemical properties of the active bed sediments, of which grain size distribution and total organic carbon (TOC) are recognized as being important factors. The presence of other contaminants, e.g. solvents, tars, oils and greases, may also be important. These may help to explain the exceptionally high bed concentrations near the Dow site. Also, since the desorption rates are generally slower than the sorption rates, the bed sediments near the Dow site may reflect the higher levels of particles at the end-of-pipe. Future models should be designed to account for the actual sorption-desorption process rather than assuming instantaneous equilibrium.

In order to improve field surveys involving sediment sampling it is suggested that: a) a fate and transport model be run and partially calibrated based on historical data before sampling plans are finalized; b) based on the predicted plume, several transects should



be selected in order to represent the longitudinal and lateral gradients for all of the dominant sources. Sampling stations within each transect should be selected at intervals that are inverse to the predicted concentration gradients; c) at each sampling station an effort should be made to sample from all the different types of deposits near the sampling point, (e.g. within 5 m of the point); d) the depth of the alluvial material should be noted; e) the physical properties of the sediments should be determined; f) the conventional chemical properties including TOC should be determined; The location, water depth, water temperature, and local current of the sampling station should be clearly indicated on a base map. An effort should be made to determine the rate of infiltration or exfiltration through the bed sediments.

#### 7.1.3 Biological Monitoring

The ecosystem sampling was an essential part of the attempt to develop a predictive model for biological responses to loads. The WASTOX food chain was used to develop such a model; however, in order to obtain a reasonable data base for calibration up to the trophic level of sportfish it was necessary to use the microcosm model previously calibrated for Mitchell's Bay and the eastern part of the St. Clair River Delta.

This calibrated model was transferred to Port Lambton and to the study site (Dow Chemical) where partial verification and prediction errors were estimated. Since the model consisted of various biotic compartments (benthic invertebrates, phytoplankton, zooplankton, benthic fish, juvenile fish, adult fish) it was possible to use the following data sets for verification:

- Sportfish (mostly Lake St. Clair)
- Juvenile fish
- Clams
- Cladophora
- Total seston

TABLE 7.1.1: UTILITY OF VARIOUS TECHNIQUES FOR ESTABLISHING EFFLUENT LIMITS

Technique	Water-Based Load Limits	Sediment-Based Load Limits	Biota-Based Load Limits
<b>EFFLUENT CHEMISTRY:</b>			
Sequential sampling	Essential A	Essential A	Essential A
Effluent chemistry: Long term monitoring	Essential B	Essential B	Essential B
Effluent toxicity	Not used A	- A	- A
<b>AMBIENT WATER CHEMISTRY:</b>			
Sequential sampling	Essential A	-	-
Investigative sampling	Essential A	Essential A	Essential A
Centrifuging	Supportive A	Essential A	Essential A
<b>BIOLOGICAL MONITORING:</b>			
Bacteria	- -	- -	- Non-essential
Benthic enumeration	-	-	Non-essential A
Contaminant residues in phytoplankton	-	Supportive B	Supportive B
Macrophytes	-	-	Non-essential A
<u>Cladophora</u>	-	-	Supportive A
Benthos	-	Supportive B	Supportive B

TABLE 7.1.1 (cont'd)

Technique	Water-Based Load Limits	Sediment-Based Load Limits	Biota-Based Load Limits
<b>BIOLOGICAL MONITORING:</b>			
Sculpins	-	-	Supportive C
Juvenile fish	Supportive C	- -	Supportive C
Sport fish	-	-	Essential C
Caged Clams	-	Essential C	Supportive B
<b>SEDIMENT SAMPLING:</b>			
Sediment chemistry	-	Essential C	Essential C
Sediment toxicity	-	-	-

Level of effort expended in study:

A = more than adequate

B = adequate

C = inadequate, more information needed

- = not used.

## 8.0 CONCLUSIONS AND RECOMMENDATIONS

### 8.1 Waste Load Allocation

- Mixing zones for the Cole drain, Polysar (Sarnia) outfalls and the Dow Chemical sewers have been delineated in accordance with Policy 5 of the MOE 'Blue Book'. Water-, sediment-, and contaminant residue in biota criteria were used to estimate allowable receiving-water-based effluent loads for all of the point sources in this study. The water-quality-based load allocations were more reliable than the sediment- and biota-based allocations due to a lower calibration error and more complete data than for both the sediment and food chain components of the model.
- As such, recommended maximum permitted loads (Table 5) were derived from the MOE Provincial Water Quality Objectives for mercury and hexachlorobenzene; water quality Advisories for OCS and 2,4,5- TCT; and criteria endorsed by outside agencies for other parameters of concern.
- The results of this study indicate that reductions in load variability would be an effective means of achieving a desired level of compliance with criteria.

The water-quality-based permitted loads may be less restrictive than biota- and sediment-based loads (e.g. Biota - HCB and OCS; sediments - Hg); however, until food-chain and sediment-based models undergo refinements, and adequate site-specific databases are developed.

It is recommended that:

- (1) The maximum allowable water-quality-based loads for specific sewers at Dow and Polysar, as well as the Cole drain (Table 5) be considered to maintain acceptable environmental conditions at the mixing zone perimeter.
- (2) Continued efforts must be expended to develop PWQOs for those parameters of concern for which there are currently no MOE endorsed Objectives. The availability of toxicity data through ongoing and proposed

government and industry initiatives will enable the development of PWQO's and PWQG's with a higher degree of confidence and more appropriate safety factors.

- (3) Additional data and model refinements be incorporated into existing food-chain and sediment-based models to:
  - i) further refine the model and
  - ii) develop biological- and sediment-based effluent limits to ensure adequate protection of the environment.
- (4) Provincial sediment quality guidelines and contaminant residue in biota guidelines require timely development to allow maximum use of sediment and biota data in fate and transport models and in determining effluent limits.
- (5) Priority consideration must be given to the development of biota-based load allocations to protect the general population, with special consideration to local communities, such as the Walpole Island First Nation Indian Community, consuming large quantities of locally caught fish.

## 8.2 Utility of Assessment Techniques for Establishing Effluent Limits

- The following assessment techniques were essential for setting water-quality-based effluent limits.
  - Ambient water sampling; Sequential sampling; Long-term effluent monitoring;
  - Juvenile fish and centrifuging data provided necessary data in support of the model calibration.
- Although the water-quality-based model is currently more reliable for setting load allocations than sediment- and biota-based models, these latter assessment techniques are necessary to determine the

effectiveness of remedial measures and will ultimately be applied with similar confidence to the present-day water-quality-based models.

### 8.3 Long-Term Effluent Monitoring

- Contaminant loadings from Dow Chemical to the St. Clair River have been substantially reduced since November 1985. Reductions between November 1985 and the 1986-87 study period were on the order of 76% for chlorinated aromatic compounds and 90% for volatile organic compounds. Before additive facility loadings can be adequately documented for the Dow complex, the effect of the re-direction of effluent streams into the Block 90 pond requires further investigation. It is recommended that:  
**Additional effluent monitoring data arising from the MISA Effluent Monitoring Regulation should be evaluated to:**
  - (i) verify sewer and facility load reductions to the St. Clair River;
  - (ii) evaluate the effectiveness of specific in-plant remedial measures;
  - (iii) assess the environmental impact of chemical discharges to the Block 90 Pond.
- Long-term effluent monitoring indicated that both the Cole drain and the Dow 42-inch sewer are significant sources of the parameters of concern, including HCB, HCB<sub>D</sub>, HCE and OCS. It is recommended that:  
**Specific remedial measures for reducing loadings of these contaminants to the St. Clair River must be undertaken in the Cole drain catchment basin and in the waste streams entering the 42-inch sewer in order to achieve the recommended water-quality-based load allocations.**

### 8.4 Sequential Sampling

- Sequential sampling demonstrated large and frequent fluctuations of chemical concentrations in all sampled sewers at Dow, Polysar (Sarnia) and the Cole drain. This may have considerable implications for the establishment of relationships between the discharged load and the resulting body burdens in biota, toxicity and criteria violations at the edge of the mixing zone. It is recommended that:



The role of load variations on chemical bioaccumulation be investigated with consideration given to the effects of pulse toxicity and/or the instantaneous uptake of contaminants by biological organisms.

- The WASTOX model was capable of reproducing the relationship between ambient concentrations and loads. Temperature differences between the river and the effluent resulted in buoyant plume effects. It is recommended that:

Buoyancy and settling effects should be incorporated in future applications using the WASTOX model.

#### 8.5 Centrifugation

- Centrifugation studies showed that HCB, HCBd and OCS were primarily sorbed to suspended solids at the point of discharge, while further downstream a larger fraction of the contaminant was in aqueous solution and therefore biologically available. At the outfall and further downstream, PERC was primarily in solution. It is recommended that: Since centrifugation is time consuming and costly, alternative methods for determining the partitioning of sorbed versus dissolved chemical should be investigated.

#### 8.6 Investigative Water Sampling

- Elevated contaminant levels in the whole water were mainly confined to a relatively narrow zone adjacent to Dow and Polysar (Sarnia); however, exceedences of the PWQO for HCB (i.e. 6.5 ng/L) occurred as far as 1200m downstream of the Dow 1st Street sewers and in 12% of all water samples. Other parameters of concern including HCBd, OCS and PERC violated water quality objectives in 0.1 to 7.8 % of samples obtained (Table 1). These exceedences occurred primarily from the Polysar (Sarnia) and Dow vicinity to Suncor.
- Model calibration and verification was difficult for some compounds, in particular volatiles, since the measured ambient water concentrations were near the method detection limit of approximately 1 µg/L (1 ppb). It is recommended that:



Research for the continued development of practical methods for low-level detection of contaminants, especially volatiles, should be encouraged.

#### 8.7. Sediment Contaminant Distribution

- Levels of various metals and organics were elevated in the vicinity of the Dow 1st Street outfalls. While sediment samples indicated a very heterogeneous matrix, levels of HCB in 1986 may be somewhat reduced over levels in 1985. It is recommended that:  
Due to the heterogeneous nature of sediments in the St. Clair River, it is recommended that a more intensive sampling effort should be undertaken. This will better document the spatial and temporal distribution of contaminants thereby improving confidence in sediment-based waste load allocation procedures and results.

#### 8.8 Sediment Toxicity

- HCB and OCS concentrations in benthic invertebrates and sediments tend to correlate. Sediments collected in the vicinity of the Dow 1st Street sewers were acutely toxic to fathead minnows and mayflies. It is recommended that:  
These parameters be given priority consideration in the development of sediment- and biologically-based guidelines. Benthic community organisms should be evaluated for use as indicators for compliance in meeting mixing zone requirements.

#### 8.9 Biological Monitoring

- At the St. Clair River Pilot Site, young-of-the-year fish were useful in the development of water-quality-based load allocations as they reflected the observed loading trends for HCB and OCS.
- Biomonitoring data indicate that the benthic community has improved substantially since the late 1970's resulting in a reduction of the "impaired" zone from 21 to 12 km downstream from the Polysar/Dow site.

Based on 1986-87 effluent loads, modelling results indicate that the impaired zone may be further reduced to approximately 6 km.

- Caged clams serve as useful biomonitors in specific areas. However, the St. Clair river has proven to be less than optimal for the recovery of introduced clams due to the river's strong currents and interference from users of the river.
- Average levels of HCB in sportfish samples collected in 1985-1987 did not exceed a human health guideline established by Health and Welfare Canada for the consumption of whole chicken eggs; however, carp and channel catfish collected from Lake St. Clair exceeded existing U.S. EPA consumption guidelines for the protection of human health.

It is recommended that:

- (1) In addition to the on-going sportfish contaminant testing program, regular biomonitoring of the benthic community and young-of-the-year fish are to be continued to document the effectiveness of further remedial measures.
- (2) The use and significance of several biomonitoring methods, which included heterotrophic bacteria, bacterial slimes, phytoplankton and macrophytes, need to be evaluated and improved by:
  - (i) Developing consistent protocols for deployment conditions, deployment times, chemical analysis considering total and bioavailable contaminant concentrations, quality assurance and monitoring of environmental variables (e.g. temperature, oxygen content).
  - (ii) Developing methods which allow a quantitative interpretation of biomonitoring results. These methods should enable body burdens in biomonitors to be translated to bioavailable chemical concentrations in the water and/or sediments, which can then be interpreted in terms of loads.

## 9.0 REFERENCES

- Abdel-Gawad, S.T. 1985. Mixing and Decay of Pollutants from Shore-Based Outfalls Discharging into Cross-Flowing Streams, Ph. D. thesis, Dept. of Civil Engineering, University of Windsor.
- Ambrose, R.B. et al. 1983. User's Manual for the Chemical Transport and Fate Model (TOXIWASP), Version 1, U.S. Environmental Protection Agency, Athens, Ga. EPA-600/3-83-005.
- Ambrose, R.B., T.A. Wool, J.P. Connolly, R.W. Schantz, 1988. WASP4 A Hydrodynamic and Water Quality Model - Model Theory, User's Manual and Programmer's Guide, USEPA, Athens, Georgia, 30613 EPA/600/3-87/039.
- Burns, L.A. Cline, D.M., and Lassiter, R. 1982. Exposure Analysis Modelling System (EXAMS), US EPA/6500/3-023, Athens, Georgia, 30613.
- CCREM 1987. Canadian Water Quality Guidelines. Prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Resource and Environment Ministers. Ottawa, Ontario.
- CESARS (Chemical Evaluation Search and Retrieval System) 1989. Produced by the Michigan Department of Natural Resources and the Ontario Ministry of the Environment.
- Chan, C.H.; Lau, Y.L.; Oliver, B.G. 1986. "Measured and Modelled Chlorinated Contaminant Distributions in St. Clair River Water", Water Poll. Res. J. Canada, Volume 21, No 3.
- Chapman, D; W. Rundle and H. Monteith 1989. Evaluation of Phosphorus Loads from Ontario Municipal Treatment Plants. Environmental Monitoring and Assessment (1). In Press.
- Connolly, J.P., R.P. Winfield, 1984. A User's Guide For WASTOX - A Framework For Modelling The Fate of Toxic Chemicals in Aquatic Environments, Manhattan College, Bronx, New York, 10471.
- Connolly, J.P., et al., 1987. A Model of PCB in the Water, Bed and Food Chain For Lake Ontario, Environmental Engineering and Science, Manhattan College, Bronx, New York, 10471.
- Corpus. 1981, 1982, 1983. Corpus Information Services Ltd. Chemical Product Profiles, Don Mills, Ontario.
- Courtney, K.D. 1979. Hexachlorobenzene (HCB): A Review. Environmental Research (20) 225-266.
- Craig, G. R.; K. Flood; J. Lee and M. Thompson 1983. Protocol to determine the acute lethality of liquid effluents to fish. Ontario Ministry of the Environment, Water Resources Branch.

- Derecki, J.A. and F.H. Quinn 1987. Use of Current Meters for Continuous Measurement of Flows in Large rivers. Water Resources Research Vol. 23 (9) 1751-1756.
- DOE/MOE 1986. St. Clair River Pollution Investigation (Sarnia Area) 135 pp. and Appendices.
- DiToro, D.M.; J.J. Fitzpatrick and R.V. Thomann, 1981. rev. 1983, Water Quality Analysis Simulation Program (WASP), and Model Verification Program (MVP) - Documentation, Hydrosience Inc., Westwood, NY, for USEPA.
- DiToro, D.M.; O'Connor, D.J.; and R. V. Thomann, 1981. rev. 1983, Water Quality Analysis Simulation Program (WASP), and Model Verification Program (MVP)- Documentation, Hydrosience Inc., Westwood, NY, for USEPA.
- Edwardson, D.C. and L. King. 1988. Upper Great Lakes Connecting Channels Study. Geographic Area Report. St. Clair River Canadian Point Sources.
- El-Shaarawi, A.H. and D.M. Dolan. 1988. Maximum Likelihood Estimation of Water Quality Concentrations from Censored Data.
- EMPPL 1987. The Effluent Monitoring Priority Pollutants List 1987. Ontario Ministry of the Environment, Hazardous Contaminants Coordination Branch. 57 pp and appendices.
- Environment Canada. 1986. St. Clair River pollution. Water Poll. Res. J. Can. 21(3):283-459.
- Environment Canada and the Ontario Ministry of the Environment, "Pollution of the St. Clair River (Sarnia Area) - A Situation Report"; November 15, 1985.
- EPA 1984. Aquatic Toxicity Tests to Characterize the Hazard of Volatile Organic Chemicals in Water: A Toxicity Data Summary. Publication No. PB84-141-506.
- EPA 1987. Guidance Manual for Assessing Human Health Risks from Chemically Contaminated Fish and Shellfish. Draft report #C737-01 for U.S. EPA office of Marine and Estuarine Protection. Prepared by PTI Environmental Services Inc.
- Fischer, H.B.; List, J.E.; Koh, R.C.Y.; Imberger, J. and N.H. Brooks. 1979. Mixing in Inland and Coastal Waters. Academic Press. Toronto. 483 pp.
- Gauch, H.G. 1982. Multivariate Analysis in Community Ecology. Cambridge University Press, Cambridge. 298 pp.
- Gobas, F.A.P.C. 1988. Personal Communication. University of Windsor, Great Lakes Institute.

- Gobas, F.A.P.C. and D. Mackay. 1989. Biosorption, Bioaccumulation and Food Chain Transfer of Organic Chemicals. Report Prepared for the Ontario Ministry of the Environment. 172 pp and Appendices.
- Great Lakes Institute 1986. A Case Study of Selected Contaminants in the Huron-Erie Corridor, Chap. 6, GLI Final Report UP-G-175, University of Windsor, Windsor, Ontario.
- Griffiths, R.W. 1978. Benthic Communities as Indicators of Water Quality in the St. Clair River. B.Sc. Thesis. University of Western Ontario, London, Ontario. 40 pp.
- Griffiths, R.W. 1985. Effect of Perchloroethylene on the Benthic Invertebrate Fauna of the St. Clair River. Prepared for the Water Resources Branch, Great Lakes Section, Ontario Ministry of the Environment, Toronto, Ontario. Prepared by Aquatic Ecostudies Limited Kitchener, Ontario. 26 pp.
- Griffiths, R.W. 1989. Environmental Quality Assessment of the St. Clair River in 1985 as Reflected by the Distribution of Benthic Invertebrate Communities. Prepared for the Water Resources Assessment Unit, Southwestern Region, Ontario Ministry of the Environment, London, Ontario. Prepared by Aquatic Ecostudies Limited, Kitchener, Ontario. ,
- GTC Geologic Testing Consultants Ltd. 1986. Regional Characterization and Waste Site Inventory. Report prepared for the Ontario Ministry of the Environment. Volume I. 256 pp. and Appendix.
- Hamdy, Y.S. and J. Kinkead 1979. Waste Dispersion in the St. Clair River. The St. Clair River Organics Study. Ontario Ministry of the Environment, Water Resources Branch. 27pp.
- Hebert, G.L. and G.A. Haffner. 1989. Habitat Partitioning and Contaminant Exposure in Forage Fish. Canadian Journal of Fisheries and Aquatic Sciences. (submitted for publication). Great Lakes Institute, University of Windsor.
- Hiltunen, J.K. and D.W. Schloesser. 1983. The Occurrence of Oil and the Distribution of Hexagenia (Ephemeroptera Ephemeridae) Nymphs in the St Marys River, Michigan and Ontario. Freshwater Invertebr. Biol. 2(4) pp 199-203.
- HSDB (Hazardous Substances Databank) 1987. National Library of Medicine. Dec. 1988.
- Hudson P.L. 1986. Personal Communication to S. Thornley MOE, Southwest Region re: 1983-1984 Macrophyte Investigation.
- IJC 1988. Spills: The Human-Machine Interface. Proceedings of the Workshops on Human Machine Interface 122 pp.
- Intera 1986. "Regional Characterization and Waste Site Inventory, Volume I.



- Jaagumagi, R. 1987. Great Lakes Benthic Enumeration Study 1985. Report to the Ontario Ministry of the Environment, Water Resources Branch.
- Johnson, G.D., and P.B. Kauss 1987. Estimated Contaminant Loadings in the St. Clair and Detroit Rivers 1984. Ontario Ministry of the Environment, Water Resources Branch, ISBN 0 7729 3264 6.
- Johnson, G.D. and P.B. Kauss. 1989. Tributary Contaminant Inputs to the St. Clair and Detroit Rivers and Lake St. Clair - 1985. Ontario Ministry of the Environment, Water Resources Branch.
- Kaminsky, R. and R.A. Hites 1984. Octachlorostyrene in Lake Ontario: Sources and Fates. Environ. Sci. Technol. (18) 275-279.
- Kauss, P.B. and Y.S. Hamdy. 1985. Biological Monitoring of Organochlorine Contaminants in the St. Clair and Detroit Rivers using introduced clams, Elliptio complanata. J. Great Lakes Res. 11(3): 247-263.
- King, L. 1987. Suggested Effluent Limitations and Control Parameters - Dow Chemical Inc. Sarnia, Ont. Environment Canada, Environmental Protection Service, Ontario Region (draft report).
- Krishnappan, B.G. and Y. Lau 1983. "RIVMIX Transport Model", Computer Programme Developed by CCIW (Canada Centre for Inland Waters) Burlington, Ontario.
- Kuehl, D.W.; K.L. Johnson; B.C. Butterworth; E.N. Leonard and G.D. Veith. 1981. Quantification of Octachlorostyrene and related compounds in Great Lakes Fish by gas chromatography-mass spectrometry. J. Great Lakes Res. (7) 330-335.
- Law, F.C.P. and R.F. Addison 1981. Response of Trout Hepatic Mixed-Function Oxidases to Experimental Feeding of Ten Known or Possible Chlorinated Environmental Contaminants. Bull. Environm. Contam. Toxicol. (27) 605-609.
- Legendre, L. and P. Legendre. 1983. Numerical Ecology. Elsevier Scientific Publishing Co., Amsterdam. 419 pp.
- Lomas, T. and G. Krantzberg. 1988. Contaminated Sediments in Great Lakes Areas of Concern. Volume II. Laboratory Sediment Bioassays. Ontario Ministry of the Environment, Water Resources Branch. ISBN 0772943370.
- McCorquodale, J.A.; E. Imam; J.K. Bewtra; Y.S. Hamdy and J.K. Kinkead, 1983. "Transport of Pollutants in Natural Streams", Can. J. of Civil Engineering, Vol 10, (1).
- McCorquodale, J.A., 1984. "Niagara River Pollution Transport", Report to the MOE, IRI 16-55.
- McCorquodale, J.A., K. Ibrahim and E. Yuen. 1986. Final report on Transport and Fate Modelling of Hexachlorobenzene in the St. Clair River. University of Windsor, IRI report #18-53 prepared for the Ontario Ministry of the Environment.

- McCorquodale, J.A., and E.M. Yuen 1987. St. Mary's River Hydrodynamic and Dispersion study. Report to MOE. IRI 18-61.
- Merck Index - 8th Edition. 1968. An Encyclopedia of Chemicals and Drugs, Merck and Co. Inc., Rathway, N.J.
- Ministry of the Environment (MOE) 1979. St. Clair River Organics Study: Biological surveys 1968 and 1977. Water Resources Assessment Unit, Technical Support Section, Southwestern Region, London, Ontario. 90 pp.
- MOE 1981a. Outlines of Analytical Methods. Laboratory Services Branch. Vols. I and II.
- MOE 1981b. The Screening of Industrial Effluents for Genotoxic Activity- The St. Clair River Organics Study. Water Resources Branch.
- MOE 1983. Ontario Drinking Water Objectives. Water Resources Branch. 56 pp.
- MOE 1984. Water Management Goals, Policies, Objectives and Implementation Procedures of the Ministry of Environment (Blue Book), Water Resources Branch.
- MOE 1985. A Guide to the Collection and Submission of Samples for Laboratory Analysis. 5th edition. Toronto, Ontario.
- MOE 1987. Preliminary report St. Clair River MISA Pilot Site Investigation Volume 1. Part 1. G.D. Johnson ed. 57 pp.
- MOE 1988a. Industrial Monitoring Information System (IMIS) Information retrievals provided by A. Radman and L. Burgess, MOE.
- MOE 1988b. Proceedings of the Workshop on Aquatic Food Chain Modelling. July 9-10, 1987. Ontario Ministry of the Environment and the University of Windsor. 177 pp.
- MOE/DOE 1988. Implementation of Recommendations of the 1986 St. Clair River Pollution Investigation Report. 30 pp.
- Mudroch, A. and Hill, K. 1987. Distribution of Mercury in Lake St. Clair and the St. Clair Sediments. National Water Research Institute Contribution No. 87-51, pp. 34.
- Munawar 1987. Personal Communication to B. Hawkins, SW Region Ontario Ministry of the Environment.
- Muncaster, B.W.; Haffner, G.D.; Innes, D.J. and P.D.N. Hebert. 1987. Biological Monitoring of Organic Contaminants in Lake St. Clair and the St. Clair River. Progress Report - November 23, 1987 to the Ontario Ministry of the Environment. Great Lakes Institute, University of Windsor.
- Nettleton, P.C. 1988. Personal Communication Ontario Ministry of the Environment, Water Resources Branch.



- Nettleton, P.C. and Y.S. Hamdy. 1988. The St. Clair River Spill Manual. Ontario Ministry of the Environment, Water Resources Branch. 57 pp.
- Neville, A. and J. B. Kennedy, 1964. "Basic Statistical Methods for Engineers and Scientists", International Textbook Co., Scranton, PA.
- Newell, A.J, D.W. Johnson and L.K. Ellen. (1987). Niagara River Biota Contamination Project: Fish Flesh Criteria for Piscivorous Wildlife. New York State Dept. of Environmental Conservation (DEC) publication.
- Niimi, A.J. and V. Palazzo. 1985. Temperature Effect on the Elimination of Pentachlorophenol, Hexachlorobenzene and Mirex by Rainbow Trout (Salmo gairdneri). Water Res. (19) pp 205-207.
- Ocean Chem 1988. Ministry of the Environment In-Place Pollutants Program Analysis of Aquatic Biota. Final Report - 1987 Program. Report prepared for the Ontario Ministry of the Environment, Water Resources Branch.
- Oliver, B.G. and Niimi, A.J. 1983. Bioconcentration of Chlorobenzene from Water by Rainbow Trout: Correlations with Partition Coefficients and Environmental Residues. Environ. Sci. Technol. (17) 287-291.
- Oliver, B.G. and Pugsley, C.W. 1986. Chlorinated contaminants in St. Clair River sediments. Water Poll. Res. J. Can. 21(3):368-379.
- Oliver, B.G. 1988. Sediment work group - Geographical area report for the St. Clair River - A level II report for the Upper Great Lakes Connecting Chemicals Study.
- Point Source Work Group 1988. "Draft One, Upper Great Lakes Connecting Channels Study."
- QSAR system 1989. Centre for Data Systems and Analysis. Montana State University On-line database. U.S. EPA and Montana State University cooperative project.
- Rastogi, A.K., and W. Rodi. 1978. "Predictions of Heat and Mass Transfer in Open Channels", J. of Hyd. Div., ASCE, Vol. 104 (3).
- Rodgers, G.K. 1986. The St. Clair River Pollution Issue. Water Poll. Res. J. Canada 21(3) 283-294.
- Rodi, W., 1980. "Turbulence Models and Their Application in Hydraulics", IAHR, Delft, The Netherlands, p. 104.
- Schloesser, D.W. and B.A. Manny. 1982. Distribution and Relative Abundance of Submerged Aquatic Macrophytes in the St. Clair - Detroit River Ecosystem. U.S. Fish and Wildlife Service, Great Lakes Fishery Laboratory. Ann Arbor, Michigan. Administrative Report 82-7.
- Schloesser, D.W., B.A. Manny and C.L. Brown. 1988. Use of low-altitude Aerial Photography to Identify Submersed Aquatic Macrophytes. In: Proceedings of the Conference on use of Remote Sensing in Plant Sciences, American Society of Photogrammetry. Contribution 643 of the Great Lakes Fishery Laboratory.

Sitwell, J. 1982. Octachlorostyrene - Draft Report.

St. Clair River Misa Pilot Site Regulatory Mixing Zone Definition:  
MEMORANDUM from G. Johnson to Peter Dennis dated November 15, 1988.

Suns, K. 1989. Personal Communication. Ontario Ministry of the  
Environment. Water Resources Branch.

Tarkpea M.; I. Hagen; G.E. Carlburg; P. Kolsaker and H. Storflor. 1985.  
Mutagenicity, Acute toxicity and Bioaccumulation Potential of Six  
chlorinated styrenes. Bull. Environ. Contam. Toxicol. (35) 525-530.

Thomann, R.V., Mueller, J.A., 1987a. "Principles of Surface Water Quality  
Modeling and Control" Harper and Row, New York.

Thomann, R.V., 1987. "A Brief Summary of an Aquatic Bioaccumulation  
Model of Organic Chemicals", Chap. 3, Proc. of the Workshop on  
Aquatic Food Chain Modelling, MOE, July, 1987.

United States Environmental Protection Agency, Environment Canada, Michigan  
Department of Natural Resources and Ontario Ministry of the  
Environment.

UGLCCS 1989. Upper Great Lakes Connecting Channels Study - Final Report.  
Management Committee. 1988. Volume II - Final Report.

Verschueren, K. 1977. Handbook of Environmental Data on Organic Chemicals.  
Van Nostrand Reinhold, Toronto 659 pp.

Wells, D.L. 1985. Tetrachloroethylene (Perchloroethylene) CAS 127-18-4.  
Chemical profile. Ontario Ministry of the Environment, Water  
Resources Branch. (unpublished report).





